FINAL REPORT

Flux Measurements of Ammonia to Estimate Emission Factors for Area Sources

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Prepared for:
Ash Lashgari
Research Division
California Air Resources Board
Research Division
1001 I Street
Sacramento, CA 95814

Prepared by:
Dennis Fitz and John Pisano
Center for Environmental Research and Technology
College of Engineering
University of California
Riverside, CA 92521
(909) 781-5791
(909) 781-5790 fax

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ABSTRACT

Emission rates from fugitive sources can be estimated by integrating the net downwind flux rate of pollutant over the height of the pollutant plume. Fluxes are measured by fast measurements at a general location of deposition in coordination with vertical wind speed measurements. Researchers from the University of California, Riverside, College of Engineering-Center for Environmental Research and Technology (CE-CERT) recently proposed using a fabric diffusion denuder to directly measure ammonia flux. Such a direct flux measurement approach would provide an inexpensive alternative to active sampling. The objective of this research was to evaluate the feasibility of determining emission factors for fugitive sources of ammonia using this passive flux sampler. The use of a fabric denuder (rather than a tubular denuder, used previously) allowed short-term sample collection periods for the measurement of ammonia flux, thus making it possible to sample during periods of prevailing daytime winds.

Emissions from five distinct sources were characterized to demonstrate that the approach is a viable method for measuring emission factors. Flux measurement obtained directly from the passive flux denuder and those calculated from an active filter-pack sampler combined with wind velocity were compared. The results show significant correlation between the two methods and invite further investigation into characterization of the passive flux denuder response. Estimation of the emission factors for the five sources were undertaken although samples were not taken at high enough elevations to determine the top of the plume. With further development and evaluation of this technique, it is possible that a larger inventory base for ambient ammonia emissions can be developed more economically than by using active samplers.

EXECUTIVE SUMMARY

Ammonia gas reacts with acidic air pollutants such as nitric and sulfuric acids to produce fine particulate ammonium nitrate and sulfate. Since these species are major contributors to $PM_{2.5}$, ammonia inventories are useful in developing $PM_{2.5}$ control strategies for airsheds that are not in compliance with this criteria air pollutant. Ammonia sources are generally fugitive in nature; the major sources are activities such as animal husbandry, application of fertilizers to agricultural fields, and sewage treatment. The emission rates are difficult to determine since ammonia is not emitted from a duct or stack. Rates from these fugitive sources are usually estimated by collecting concentration and wind speed data as a function of elevation and multiplying them together to produce a flux. Using the mass balance approach, emissions are estimated by integrating the net downwind flux rate of pollutant over the height of the pollutant plume. The emission rate per area of is found by dividing by the fetch of the source. These measurements are expensive to perform and, therefore, few data exist for fugitive ammonia emission factors.

A passive diffusion denuder has been reported in the peer-reviewed literature that can be used to make flux measurements directly without any sampling pumps or wind data. A major limitation of this approach was the tubular design that severely limited the flow through the denuder; this required long sampling times. Sampling time of several days were needed for typical sources. This limited the amount of data that could be collected, made it impossible to quantify the effects of meteorology, and required that sampling be stopped when the wind direction reversed in order to focus on a single source.

Researchers at the University of California, Riverside, College of Engineering-Center for Environmental Research and Technology (CE-CERT) recently developed a fabric diffusion denuder that would allow for a much higher sampling rate for passive sampling. Such an approach would provide an inexpensive alternative to active sampling and provide a direct flux measurement. The objective of this research was to evaluate the feasibility of using this passive flux sampler for determining emission factors for fugitive sources of ammonia. The use of a fabric denuder (rather than a tubular denuder used previously) allowed short-term sample collection periods for the measurement of ammonia flux, thus making it possible to sample during periods of prevailing daytime winds. The research involved the following steps:

- Design a passive flux sampler based on the fabric denuder.
- Field measurements of five separate types of fugitive sources of ammonia.
- Comparison of NH_3 fluxes determined by passive flux denuders with those determined from active sampling.
- Estimation of NH_3 emission factors from the fugitive sources investigated.

- Evaluation of the feasibility and future development of the method.

An open-face Savillex Teflon filter holder was used to hold a pair of fabric denuders. Instead of an outlet to a pumping system, an open outlet was used to attach the holder to a section of 1½-inch PVC pipe which has been machined to fit the open outlet. The other end of the PVC pipe was fitted with a similar pair of denuders for characterizing the denuder blank concentrations. No flow restriction device was necessary. Sample collection depended on the wind flowing through the assembly. The amount of ammonia collected, therefore, was proportional to the wind speed, direction, and ammonia concentration. Only a single tube would be required if it faced directly into the wind and either the wind direction was invariant or the tube was mounted on a wind vane. When the tube is stationary and the wind is varying, an additional tube mounted at a right angle would be needed to characterize these vector components of the flux. Figure ES-1 shows a schematic of a single tube sampler in a north-south axis orientation.

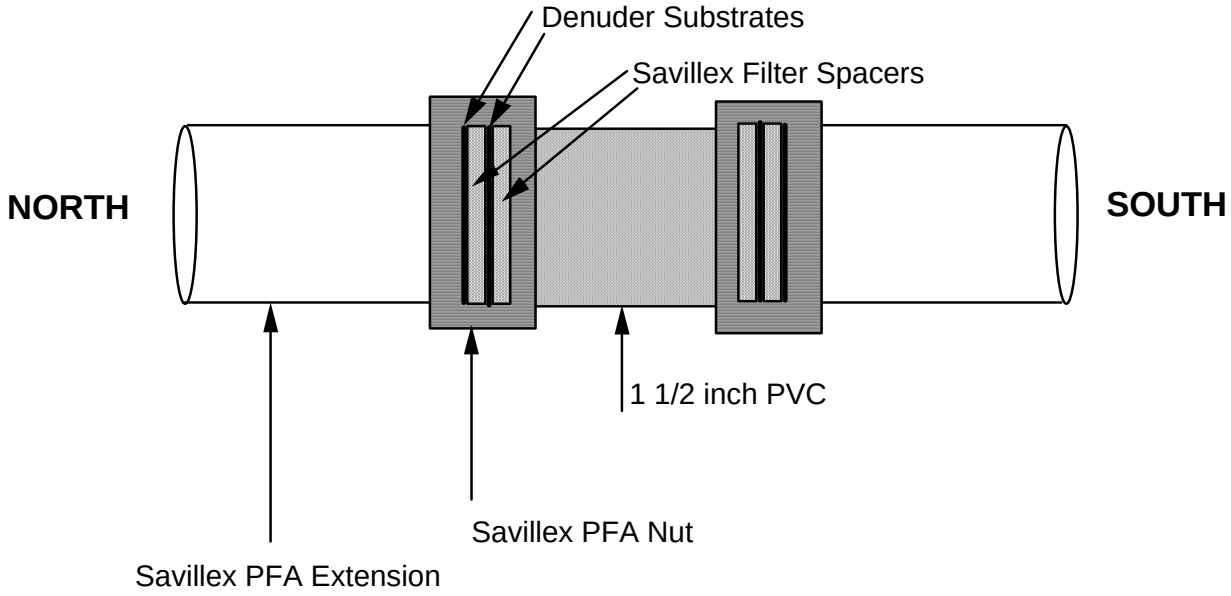

Figure ES-1. North-south passive flux sampler using fabric denuders.

The fugitive sources included a dairy farm, a dairy lagoon (with and without acidification), a pig farm, and two fertilized fields (one fertilized with urea, the other with dairy lagoon effluent). A sampling tower up to 13 m high was used downwind of the sources with measurements made at up to five elevations. Additional single-elevation towers were placed either to the side of the main tower (to evaluate homogeneity of the source) or further downwind (to evaluate dispersion modeling of the NH_3 plume).

Samples were collected for two to three hours during periods of consistent wind speed and direction. Passive samplers were used as described above with the fabric coated with a 9%

phosphoric acid solution. The active samplers consisted of a filter pack with a Teflon front filter followed by a citric acid impregnated cellulose back filter. These were also mounted in a 47mm open-face Savillex Teflon filter holder. The active samples were operated at 9 L/min. All samples were extracted in deionized water, and the ammonia quantified using the indophenol blue colorimetric method.

Collocated sampling was used to estimate the precision of the passive flux measurements. The two samplers were highly correlated with a least squares correlation coefficient squared of 0.984. The relative standard deviation between the two collocated samples for the 32 denuders was 0.21. In all cases the passive denuders facing the wind collected the major amount of ammonia. The ammonium on the denuders facing at a right angle to the wind was very low, near that of the denuder blank in many cases. The concentration of ammonium on the lowest pair of denuders (which invariably faced a direction at a right angle to that of the wind) was subtracted from the other denuders as this represented ammonia collected from passive sampling without flow (it therefore did not represent a flux). The collection efficiency of the passive denuders facing the wind (which collected significant amounts of ammonia compared with the denuder blank) was generally 90%, in good agreement with the efficiency previously found for active denuders.

The ammonia flux through the denuders was calculated by dividing the ammonium on the denuders by the area of the denuder and the time of sampling. This was compared with the flux from the collocated active samplers, which was calculated by multiplying the ammonia concentration by the wind speed. Figure ES-2 shows the least squares plot between the two methods for all of the data we collected. The two methods are highly correlated, with a coefficient squared of 0.83. We do not expect perfect correlation because the methods are different, and because the passive denuder measures flux directly while the calculation method assumes that the wind speed is constant when it is, in fact, variable. The slope of the regression, however, is 0.051, with the flux calculated by the passive denuder being much lower.

We expected that the air flow through the denuder would be lower than that of freely moving air. To evaluate the difference we set up a wind tunnel and measured the wind speed both in the denuder and outside of it. The relationship was linear up to a speed of 7 m/s with the air speed inside the denuder eleven times smaller. This accounts for over half of the discrepancy with the active sampler. Turbulence due to the denuder being at an angle to the wind (in the wind tunnel test the denuder faced directly into the wind) may also account for some of the remaining discrepancy.

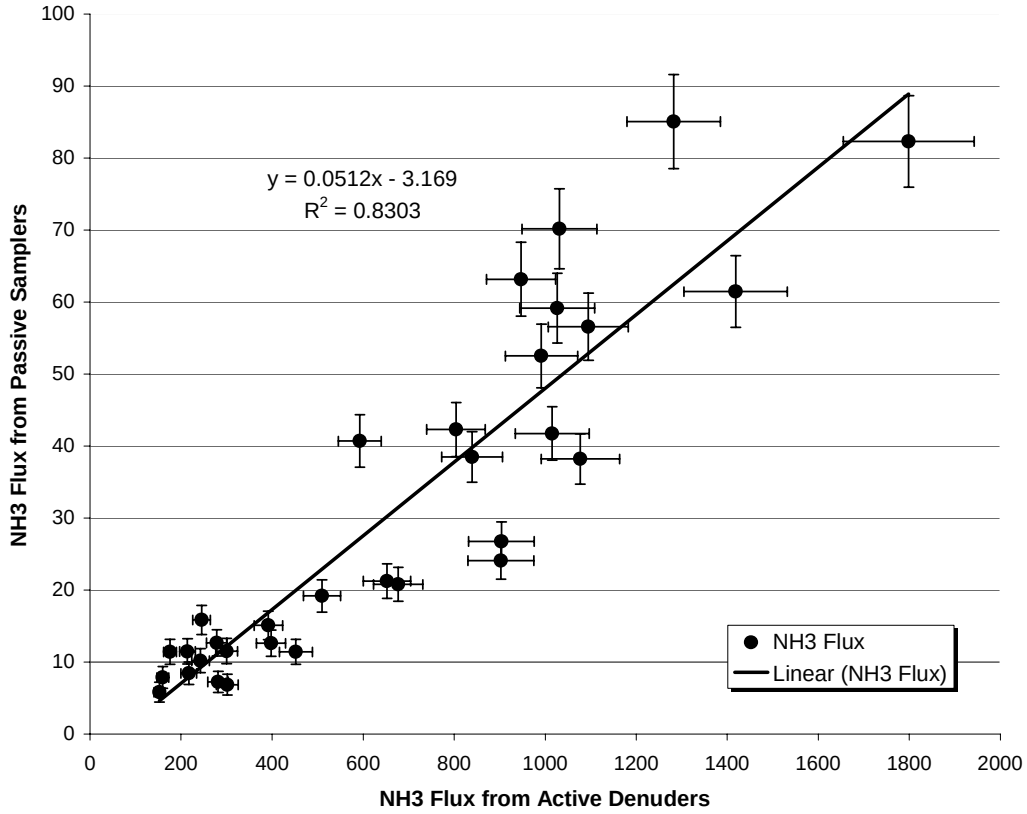

Figure ES-2. Linear regression plot comparing the flux measured with the active sampler with the passive flux sampler for all 32 measurements made.

Emission factors determined from the active samplers ranged from 1-10 μg/cm^2-min. these are in general agreement with emission factors determined by others. The emission factors from the passive sampling would need to be multiplied by 20 to achieve these values.

The passive flux denuder was shown to be an economical method of measuring NH_3 emission rates that was comparable to measurements made with an active sampler. Future work should consider mounting the denuder on a wind vane. The ammonium collected on the downwind side would be representative of passive sampling of concentration without wind and would be subtracted from the ammonium on the side facing the wind. This arrangement requires four denuders rather than eight per sample. In addition, both the front and back denuders could be co-extracted and analyzed together since breakthrough does not appear to be significant. This vane approach should again be compared with flux measured using active samplers to determine if the remaining discrepancy between the two methods can be resolved.

1.0 INTRODUCTION

Ammonia (NH_3) is an important trace constituent of the lower troposphere. It is the dominant gaseous base and is responsible for determining the level of atmospheric acidity (Erisman et al., 1988). The role that ammonia plays in neutralizing acidic aerosols has led to many studies concerning health effects of atmospheric aerosols (Seinfeld, 1986; Harrison, 1993). Higher local emissions of NH_3 result in the enhancement of aerosol formation that ultimately result in the following:

1) Formation of ammonium nitrate (NH_4NO_3) by reacting with HNO_3.
2) Formation of sulfate as the increase in pH enhances the rate of oxidation of dissolved sulfur dioxide by ozone (Asman and Janssen, 1987).
3) Formation of either ammonium sulfate (NH_4HSO_4), or ammonium bisulfate ($(NH_4)_2SO_4$) by neutralization of sulfuric acid (Brost et al., 1988).
4) Formation of ammonium chloride by reacting with HCl (Finlayson-Pitts and Pitts, 1996).

NH_3 has a lifetime usually of 1-5 days (Warneck, 1988), but once transformed to ammonium aerosol has an atmospheric lifetime that increases by at least a factor of 3 (Aneja et al., 1998). This allows for more widespread pertubation of soil acidity as well as direct deposition to plants resulting in excess nitrogen. Excess nitrogen is known to enhance the replacement of slow-growing plant species with fast-growing grass species (Heil and Bruggink, 1987), causing adverse effects on many types of plant vegetation. In coastal areas excess nitrogen alters the growing frequencies of both toxic and non-toxic phytoplanktron, seriously affecting this delicate ecosystem (Pearl, 1995). Increased production of ammonium aerosol also enhances light scattering as the increase in the size of the aerosol generates higher light scattering efficiency. This results in visibility degradation (Sisler and Malm, 1994).

It is known that the largest contributor of ammonia to the global budget is domestic animal waste, as from dairy, cattle and swine farms (Bouwman et al., 1997). Although there is now increased concern about NH_3 emissions from mobile sources, there is still a strong need to evaluate domestic waste sources. California is ranked highest in U.S. milk production, producing 26 billion pounds of milk and cheese (CDFA, 1999). In 1998, livestock cash receipts totaled $6.85 billion, due mainly to increased milk and cream sales (CDFA, 1999). While the growth of this industry has resulted in significant economic returns for the state, there is the issue of effective manure management. As much as 40% of feed dry matter fed to the animals can be

excreted in the manure, requiring a significant amount of labor and capital investment for manure management and disposal (Zhang, 1999). In dairy operations, manure is commonly handled as an effluent stream of liquid or slurry manure by means of a hydraulic flushing – lagoon storage – irrigation system. A significant consideration associated with manure management is the loss of ammonia produced during the decomposition of manure in storage lagoons.

Between 80 and 200 different gases have been identified during the decomposition of manure (Sheffield, 1998). Of these gases, NH_3 is of primary concern because of: (a) the health issues related to particulate matter (PM) formation and (b) the loss of important plant nutrients from the manure. For example, NH_3 is volatilized from lagoons, whereby the valuable ammonium ion (NH_4^+) is lost as NH_3 (Powlson, 1993). Volatilized NH_3 can react in the atmosphere to produce ammonium nitrate or ammonium sulfate and thereby contribute to airborne particulate matter (PM). The California Air Resources Board (ARB) has developed preliminary emissions inventories for NH_3 from most potential sources in the state (Gaffney and Shimp, 1999), all of which were reported with high initial uncertainties for source contributions. In the urban environment of California, ammonium nitrate accounts for 30-60% of the fine aerosol mass. The Federal government and the State of California have established ambient air quality standards for particulate matter with aerodynamic diameters of both 10 μm or less (PM_{10}) and 2.5 μm or less ($PM_{2.5}$), which invites further concern about the overall ammonia contribution to the fine aerosol mass.

As a result of the health, environmental, economic and regulatory concerns, there is a need to quantify NH_3 emissions at dairies and pig farms. Since NH_3 is one of the by-products of microbial degradation of manure and organic matter, ammonia emission from this process can be directly measured by investigating gas emissions from dairy lagoons, where the manure is stored in aerobic or anaerobic conditions (Zhang, 2001). In addition, gaseous emissions from these lagoons are influenced by climatic factors such as wind speed, temperature, humidity and precipitation (Sheffield, 1998; Walter et al., 1999), as well as the pH of the dairy effluent (Zhang, 2001). For example, acidification of cattle slurry applied to grasslands has been used to reduce NH_3 emission rates (Bussink et al., 1994).

1.1 Objectives

The objective of this study was to evaluate whether emission factors from fugitive sources of ammonia can be achieved using a passive flux sampler based on a high-capacity fabric denuder. To carry out this feasibility study the following steps were done:

- Design of a passive flux sampler using fabric denuders.
- Field measurements of five independent sources of ammonia using the passive flux samplers.
- Comparison of NH_3 fluxes determined by passive flux denuders with those determined by an active sampling technique.
- Estimation of NH_3 emissions from the fugitive sources investigated.
- Analysis of the technique and projection of feasibility as well as future work required for improvement and validation.

1.2 Fabric Denuders

Diffusion denuders have been developed to sample air pollutants that are semi-volatile such as ammonium nitrate, which is a solid particle in equilibrium with ammonia and nitric acid vapor. These devices selectively and irreversibly remove the gas phase components while allowing particles to pass unattenuated. Diffusion denuders were first constructed as tubing bundles (Shaw et al., 1982), progressed to annular geometries (Possanzini et al., 1983; Allegrini et al., 1987), and then to honeycomb structures (Koutrakis et al., 1993). Fitz and Motallebi (2000) recently reported the successful use of fabric denuders to selectively remove nitric acid. The denuder sampling approach they proposed is based on diffusion research for devices used to remove very fine particles that preceded the development of diffusion denuders for removing gases. These devices, known as diffusion batteries, are used to size-resolve submicron particles *in-situ.* They were originally constructed using a single long channel, then using tubing bundles they became

more compact, but also more complex to fabricate. These eventually evolved to honeycomb structures, and finally wire screens (Sinclair, 1986). This development is analogous to the development of diffusion denuders for sampling semi-volatile species. The use of cloth fabric as the denuder substrate, therefore, is analogous to the wire screen denuders for collecting very fine particles in diffusion batteries. The finer the mesh, the greater the deposition will be by either particles or gases. In the case of particles, the wire of the mesh is typically 10 μm in diameter with a spacing of 20-50 μm.

Typically, more than 100 such screens are necessary to remove submicron-sized particles. Since the diffusion coefficient for gases is several orders of magnitude higher than for particulate matter, a single screen, which need not be as fine, could be used. Cloth, with a typical thread size of 100 μm spaced on centers of 250 μm, leaving an open grid of 150 μm, would be sufficient. To estimate removal efficiency, comparisons to theoretically calculated values using the theory developed for wire diffusion screens (Cheng et al., 1980) were conducted. Fabric denuders were first evaluated by looking at the removal efficiency of HNO_3 by Na_2CO_3 coated examples (Fitz and Motallebi, 2000).

The feasibility of the concept was first evaluated by using the theory developed for wire diffusion screens (Cheng and Yeh, 1980). By assuming a denuder is treated with a chemical that quantitatively removes a target gas upon contact with the denuder surface, the theoretical denuder efficiency can be determined from the equation to describe the fractional penetration of a particle (P) which is given by

$$P=\exp(-AnPe^{-2/3}) \qquad (1)$$

where:

$$A = \frac{2\beta ah}{\pi(1-a)r}$$

with:

ß = 2.7

a = solid surface fraction = 0.345

r = fiber radius in cm

h = screen thickness in cm

n = number of screens

P_e = Peclet number = $2r\ U_{0/D}$

where:

U_0 = undisturbed flow velocity

D = diffusion coefficient

For example, to apply this equation to nitric acid, for a 4.0 cm diameter cloth sampling at 10 L/min, the dimensions of the cloth grid cell and the diffusion constant for nitric acid at room temperature, 0.12 cm^2/sec are used. This results in a penetration of 0.02 or 2%. On the other hand, using the diffusion coefficient of a 0.1µm particle (6×10^{-6} cm^2/sec) results in a penetration of greater than 99%. Since cloth substrates had not previously been used as gaseous diffusion denuders, laboratory testing was needed to optimize the denuder geometry and coating material. Fitz and Motallebi (2000) observed that they could estimate denuder efficiency by estimating the fractional penetration of the gas and assume that the denuder is treated with a chemical that quantitatively removes a target gas, when the gas in question comes in contact with the denuder surface. They concluded that two denuders made of a cotton fabric, 47 mm in diameter, were required in series to ensure a collection of over 95% of the HNO_3 acid in ambient air when sampling up to 10 L/min.

2.0 MATERIALS AND METHODS

2.1 Ammonia Removal by Fabric Denuders

The efficiency of ammonia removal by using phosphoric acid as the coating material was investigated by Fitz and Tuazon (2001), as part of their work reported in the final report to ARB under Contract No 94-338, "Evaluation of a Sampling Methodology for Acidic Species."

In that project, denuders were evaluated in the laboratory by passing known concentrations of ammonia (NH_3) through them at various temperatures and humidities. Ammonia concentrations were generated using commercial permeation tubes with specified emission rates. Gas mixtures in the range of 10-40 ppb were generated at relative humidities of 10-80%. Concentration measurements, used to determine penetration, were made before and after the denuder. The concentration of ammonia was monitored by reducing NH_3 to NO by passing the sample through a high-temperature stainless steel converter and then measuring the NO concentration with a commercial chemiluminescent NO analyzer. Denuders coated with 2% phosphoric acid and with 9% phosphoric acid were tested for collection of ammonia. Table 2-1 shows a summary of the their results of testing phosphoric acid coated fabric denuders. Overall, the collection efficiency of a single 9% phosphoric acid denuder is better than 90%, and two denuders used in series would have better than 99% collection. The passive flux sampler, therefore, was designed incorporating two separate denuders in series for each direction.

Table 2-1. Phosphoric acid coated fabric denuder efficiency.

	Nominal Conc. ppb	Temp ºC	RH %	Duration days	Flow rate L/min	Denuder Coating (w/w)	Collection efficiency %
NH_3	**38**	**21**	**17**	**0.9**	**2**	**2% phosphoric**	**66**
NH_3	**38**	**20**	**20**	**1.8**	**2**	**9% phosphoric**	**90**
NH_3	**40**	**38**	**20**	**2.7**	**2**	**9% phosphoric**	**95**
NH_3	**15**	**21**	**20**	**1.1**	**2**	**9% phosphoric**	**100**
NH_3	**15**	**21**	**80**	**7.0**	**2**	**9% phosphoric**	**100**
NH_3	**13**	**38**	**22**	**4.9**	**2**	**9% phosphoric**	**100**

2.2 Procedures for Ammonia Analysis from Fabric Denuders

Since this project required the analysis of more than 700 individual fabric denuders, a standard method for their analysis was written. This method was applied to all fabric denuders analyzed and was carried out by only two individuals so as to maintain consistency. This aspect of the analysis proved to be very successful as test samples were included from each site and found to be consistent under analysis. The actual SOP for the denuder analysis is included as Appendix A.

2.2.1 Reagent Preparation

The indophenol reagent is made by first preparing the buffer solution: 15 g of sodium phosphate, 15 g of sodium citrate tribasic, and 1.5 g of EDTA are added to a Class A 500 mL volumetric flask. The flask is filled with deionized water to the line. The indophenol reagent is then made by adding 30 g of phenol and 0.1 g of sodium nitroprusside to 450 mL of the buffer solution. After the phenol is dissolved, the 500 mL volumetric flask is filled to the line with the remaining buffer solution. The indophenol reagent is stored in a dark bottle in a refrigerator. Next, a 1N sodium hydroxide solution is made by dissolving 20 g of sodium hydroxide in water in a 500 mL flask. 30mL of commercial bleach is dissolved in 400 mL of the sodium hydroxide solution. This was diluted to 1000 mL in a volumetric flask to make the alkaline hypochlorite reagent.

2.2.2 Standards

The ammonia nitrogen reference standard, 1000 mg/L, is made by dissolving 3.819 g of dried ammonium chloride in a 1000 mL flask filled with water. The ammonia nitrogen standard, 10 mg/L, is made by diluting 10 mL of the reference standard to 1000 mL. An intermediate ammonia nitrogen standard,1 mg/L, is made by diluting 10mL of the standard to 100 mL.

Six standard solutions are made from the intermediate standard. Each of the six beakers receives 0, 2, 4, 6, 8, or 10 mL of the intermediate solution. Then each beaker is diluted to 10mL total with water. 4.0 mL of the indophenol reagent and 6.0 mL of the alkaline hypochlorite reagent are added to each beaker. The beakers are swirled and set aside for 45 min. After this time, each solution is transferred to a cuvette and measured three times in a spectrophotometer set at wavelength 635 nm.

2.2.3 Sample Analysis

The filter samples are extracted by adding 10 mL of DI water to the centrifuge tube with the filter inside and sealed. The centrifuge tubes are placed on a shaker table for an hour. After this time, the solutions from each tube are poured into beakers and 4.0 mL of the indophenol reagent and 6.0 mL of the alkaline hypochlorite reagent are added to each beaker. After 45 minutes, each of these sample solutions are also analyzed by the spectrophotometer at a wavelength of 635 nm. Any sample with an absorbance reading of greater than 1.00 was diluted and tested again.

2.3 Passive Diffusion Denuder Construction

The passive flux sampler design is based on the approach used by Schjoerring (1995), but, instead of using denuder tubes, the design was modified to use 47mm fabric denuders. Like filter types of active samplers, an open-face Savillex Teflon filter holder is used to locate a pair of fabric denuders. However, instead of an outlet to a pumping system, an open outlet is used. This open outlet was made from a section of machined 50mm PVC pipe. The other end of the PVC pipe is fitted with a similar pair of denuders, so there is symmetry on both sides of the center axis through the PVC pipe. No flow restriction device was necessary.

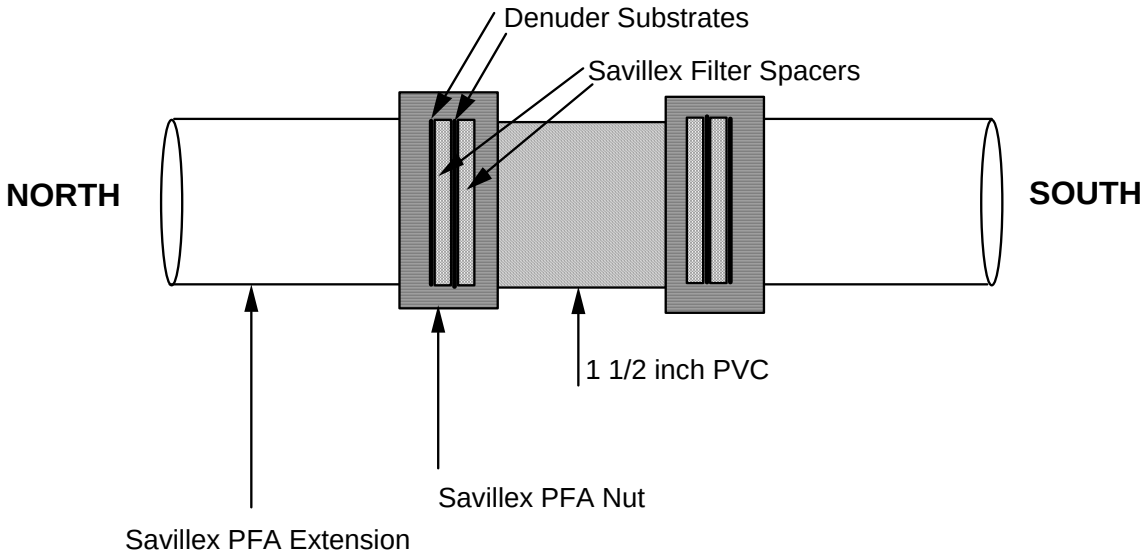

Figure 2-1. North-south passive sampler using 4 fabric denuders.

Sample collection depends on the wind flowing through the assembly. The amount of ammonia collected, therefore, is proportional to the wind speed, direction, and ammonia concentration. To measure the flux at a point, two such samplers are needed; one on an east-west axis, the other on

a north-south axis. Figure 2-1 shows a schematic of this sampler in a north-south axis orientation. Figure 2-2 shows the installation of the passive sampler on the meteorological tower. The tower employed for the study was capable of sampling to elevations as high as 20 m. For most of the sampling episodes, elevations up to 10 m were employed.

Figure 2-2. Installation of passive sampler on meteorological tower.

2.4 Passive Denuder Flow Testing

An experiment was conducted to examine the flow abatement through the passive denuder assembly. A variable-speed blower was used to simulate wind speeds from 2 to 7 m/sec. The laminar flow output from the blower was sufficiently large enough in diameter so as to encompass the front surface area (47 mm) of the denuder assembly. The simulated wind speed was measured with a Dwyer Wind Meter. The pressure drop inside between the pair of north to south or east to west fabric denuders was calibrated for different flows by using a manometer. This allowed determining the flow versus pressure response of the denuder assembly. This could be related to the bulk air speed past the denuder. Measurements were then made of the pressure drop inside the denuder assembly for various air speeds generated by the blower. A plot of the

two in Figure 2-3 shows that the flow through the denuder is linearly reduced by approximately a factor of 11. Since these tests were done under ideal conditions, where the air was blown directly on the front face of the denuder assembly and neglecting the turbulent and directional changes in field conditions, this can only be used as an approximation. Further work needs to be done to investigate the flow abatement through the denuder as a function not only of wind speed, but also of turbulence and wind direction.

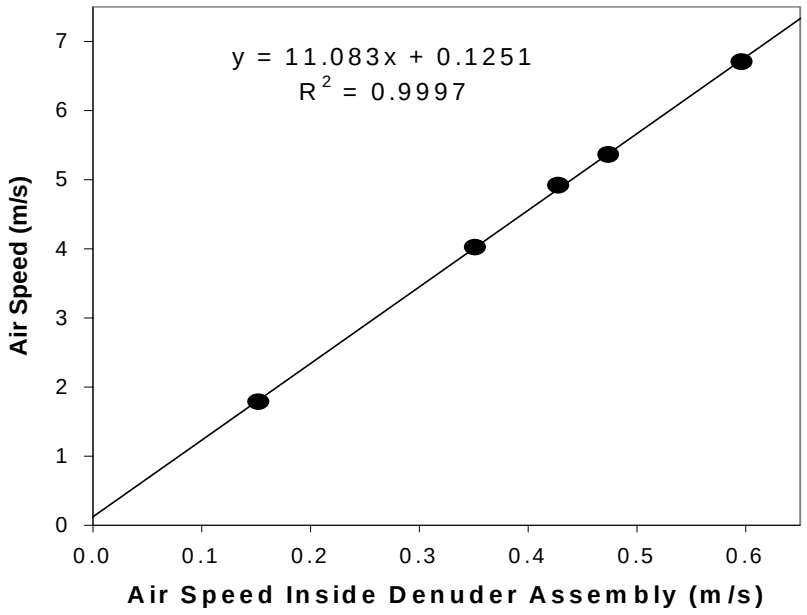

Figure 2-3. Plot of flow abatement through the passive denuder assembly.

2.5 Site Selection

2.5.1 Citrus Grove

A citrus grove at the University of California, Riverside, was chosen for investigating emissions from an agricultural field. The site is located in the Agricultural Operations in Riverside south of Martin Luther King Boulevard between Chicago and Canyon Crest avenues (Figure 2-4). The site was chosen because it was going to be fertilized with urea 46-0-0 fertilizer at rate of 230 lbs./acre. Sampling was taken the day after the application. A meteorological tower was placed downwind of the citrus grove. The grove has approximate dimensions of 400 by 230 meters. The sampling tower was located on the road at the midpoint between 13-B and 13-C. An upwind sample was located exactly due west of the sampling tower on the western side of Chicago Avenue.

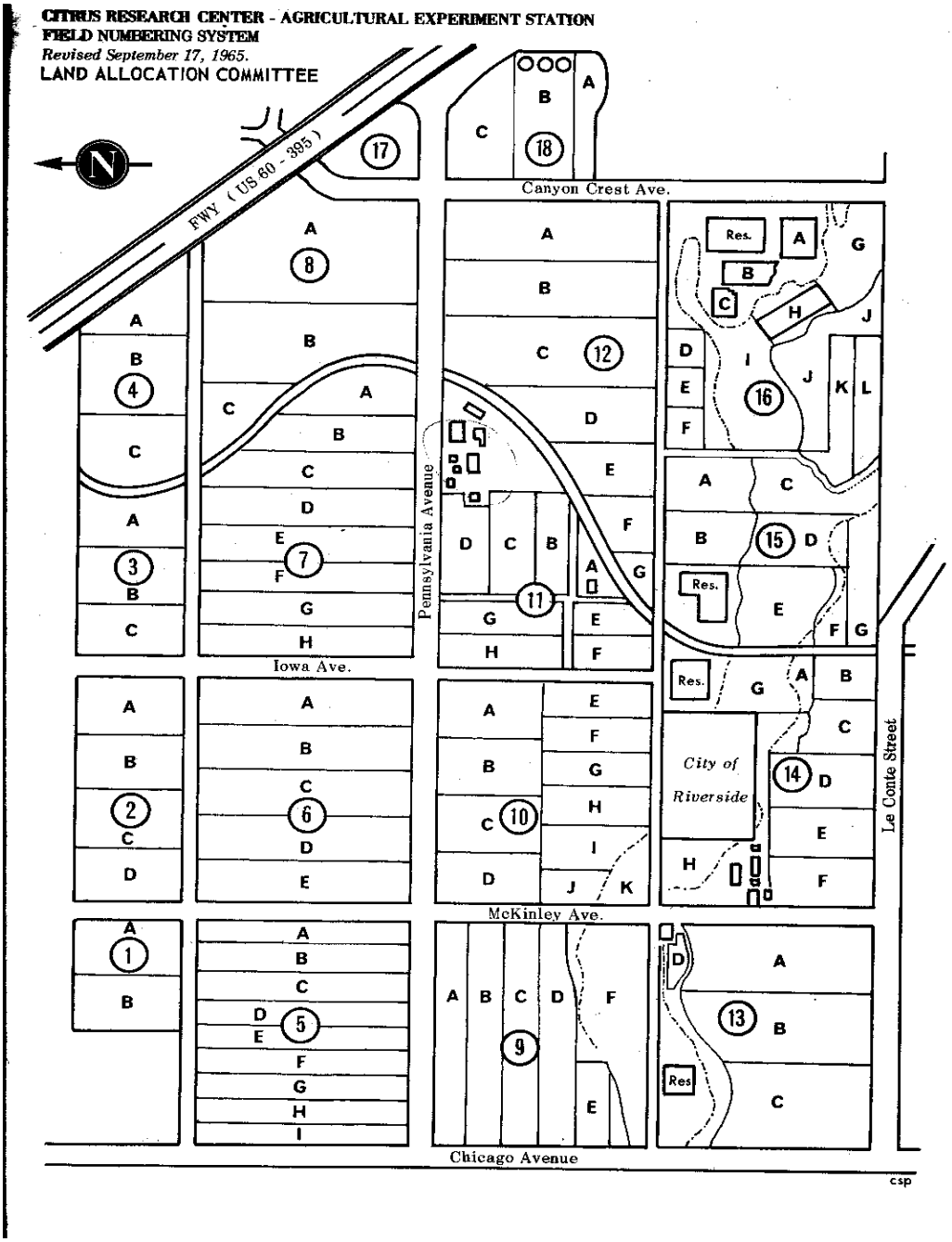

Figure 2-4. Map of the Citrus Research Center. Note the figure is oriented with east at the top and north at the left. The citrus grove measured was 13-C, which is located at the bottom right on the figure bordering the southwestern edge of the grove as outlined from the intersection of Chicago Avenue and Le Conte Street.

2.5.2 Dairy Farm

A medium-sized dairy operation (500 head) at California State University, Fresno, was selected because we were able to conduct controlled measurements there and include emissions from the

adjacent dairy lagoon (Figure 2-5). With the lagoon directly north of the dairy farm, the tower was mounted in the southeast corner just in front of the tree line near the roadway.

Figure 2-5. Aerial photograph of the Fresno Stae dairy operation. The farm, the stall areas, open containment area, and the lagoon are visible.

The inclusion of emissions from the dairy farm as well as the lagoon was to eventually provide emission estimates for total dairy operation. The investigation of the lagoon was scheduled to coincide with CIT's (Center of Irrigation Technology) separate investigation into lagoon acidification practices to investigate dairy lagoon emissions from non-acidified lagoons and acidified lagoons. This also provided the best opportunity to compare the passive samplers with corresponding active samplers. The dairy farm required six sets of passive denuders. Since the prevailing winds are from the northwest, the sampling tower was selected to be approximately 100 m downwind of the dairy with passive denuders at 1 m, 2 m (two at this elevation) and 5 m. The collocated sample set was used to estimate the overall precision of the measurement. An upwind sample and another sample another 100 m downwind, both at 1 m elevation, completed the six sample sets. A total of 48 denuders were required for each sampling day, with two days sampled. The lagoon was located due north of the dairy and at a distance far enough from the dairy farm itself to be considered independent. Climatic conditions during monitoring of NH_3

emissions at the dairy farm are presented in the comparison with the active sampling in Section 4-3 of this report.

2.5.3 Dairy Lagoon

The lagoon required three sets of passive denuders. Since the prevailing winds are also from the northwest, the sampling tower was directly southeast of the primary lagoon. The samplers, both active and passive, as well as individual meteorological sensors, were set at 1 m, 2 m and 5 m elevation. An upwind sample at 1 m completed the four sample sets. A total of 32 denuders were required for each of three sampling days. It was agreed to minimize flow variation through the passive denuders that sampling would be conducted during the time of day when winds were consistently from a single direction. This was generally the case for the sampling episodes as sampling times were kept between three and four hours during the early afternoon when the winds were the most stable. Two field blanks were taken for each sampling period. Climatic conditions during monitoring of NH_3 emissions at the lagoon are also presented in the comparison with the active sampling in Section 4-3.

2.5.4 Pig Farm

Due to the success of the measurement program of the dairy farm and the dairy lagoon with Fresno State University, the next two sampling sites were also located in Fresno. The first was the pig farm at Fresno State. The pig farm sampling location was far enough away to be deemed independent of the dairy operation. The lower part of the pig farm can be seen on the left side of Figure 2-5; it is south and west of the dairy.

There has been considerable research in investigating the effects of NH_3 emissions from pig farms (Beauchamp et al., 1982; Zhang et al., 1997). Sampling locations were selected for the pig farm at two locations. The pig farm measurement program used 8 sets of passive denuders. Since the prevailing winds are from the northwest, the sampling tower was selected to be approximately 50 m downwind of the pig farm with passive denuders at 1 m, 2 m, 5 m, and 10 m. An upwind sample and another set of three passive denuders on a second tower another 75 m downwind (125 m total) completed the eight sets. The second tower had sampling elevations at 1 m, 2 m, and 5 m. A total of 64 denuders were required for each sampling day, with only a single

day measured. Climatic conditions during monitoring of NH_3 emissions at the pig farm are presented in the comparison with the active sampling in Section 4-3.

2.5.5 Fertilized Field

Since we had made dairy lagoon measurements, it seemed interesting to see what the emissions would be when the dairy lagoon effluent is used to fertilize a nearby farm, a common practice (UCCE, 2000). The field had dimensions of approximately 300 by 300 m. The fertilizer application measurement program also required 8 sets of passive denuders. Since the prevailing winds are from the northwest, the sampling tower was selected to be approximately at the center of the fertilized field. There at the field center the tower was installed with passive denuders at 1 m, 2 m, 5 m, and 10 m. Another denuder was placed at the extreme northwest end of the field. This would be used as the upwind sample. At the location where the effluent entered the field, which was at the southeast end of the field, another set of three passive denuders on a second tower approximately 150 m from the field center tower were installed. Climatic conditions during monitoring of NH_3 emissions over the two sampling days at the fertilized field are presented in the comparison with the active sampling in Section 4-3.

The location of the two sampling towers is shown in Figure 2-6, which depicts the lagoon effluent fertilized field. The small tower is in front with a 2 m tripod adjacent to it. This tripod provided the mounting necessary for the active samplers. Figure 2-7 shows the lagoon effluent source and its distribution over the fertilized field. The small tower had sampling elevations at 1 m, 2 m, and 5 m. A total of 64 denuders were taken for each of the two sampling days. The location of the fertilized field was far enough away to be deemed independent of the dairy operation, the lagoon itself, and any other ammonia emitting sources.

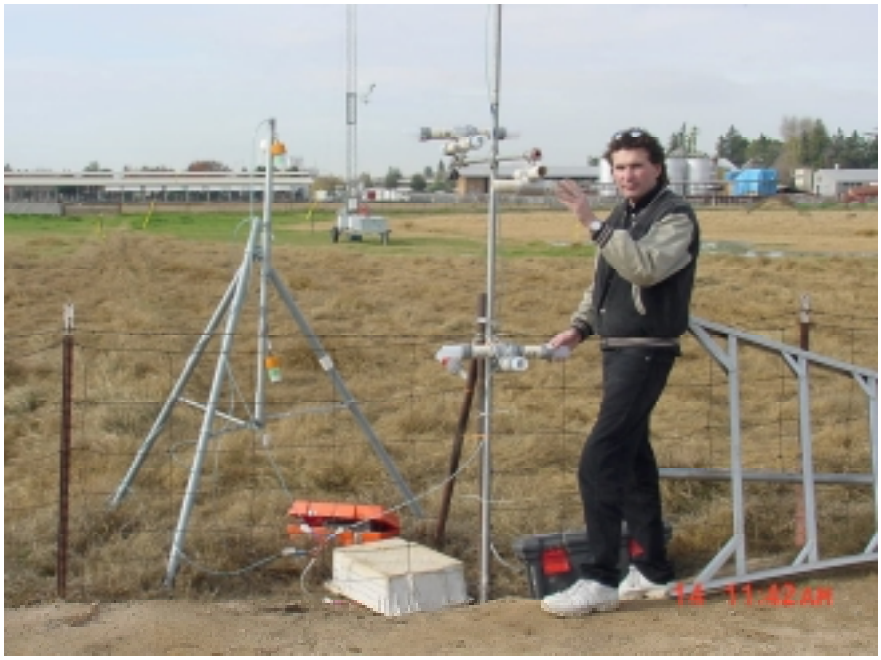

Figure 2-6. Two towers used during fertilized field sampling.

Figure 2-7. Lagoon effluent source and subsequent distribution over the fertilized field.

2.6 Collaboration with the California State University, Fresno

Due to the dairy and pig operations at California State University at Fresno and the fact that ammonia emission measurements of these operations were being conducted by Dave Goorahoo and Charles Krauter, both of CSUF, we decided that we could best evaluate the passive flux sampling technique by coordinating our experimental program and collaborating with them. It was also during that time that they were conducting an investigation of what has become a more commonplace dairy practice, the acidifcation of the dairy lagoon.

This allowed us the opportunity to investigate whether the emission rate from a fugitive emission source such as a dairy lagoon could be evaluated by the passive flux sampling technique. Their research is primarily measuring ammonia emission rates using active samplers and dispersion modeling. The acidification of the dairy lagoon also provided us the opportunity to measure what we expected would be significant changes in NH_3 emissions over a short-term period as the experiment was just over three consecutive days.

In effect by collaborating with CSUF, this allowed for repeated measurements of emission rates over the sites investigated. We were able to do three independent sets at the dairy lagoon and two at the dairy farm. We also were able to investigate the fertilizer application of the dairy lagoon effluent into a nearby fertilized field.

2.7 Meteorological Data

A 20 m meteorological tower (Figure 2-8) was employed for the field measurements. For the work done in conjunction with Fresno State, meteorological sensors were placed at 1, 2, 5, 10, and 20 m elevation. RM Young AQ wind speed/direction and temperature sensors were used.

A Vaisala model AMP23UA sensor was used to record relative humidity. Temperature and RH were determined at a single level. Wind speed and direction were measured at the all the levels.

The wind anemometers were calibrated by attaching a synchronous motor to the cup shaft as described in the manual. Factory conversion factors to convert rpm to speed were used to generate a calibration curve by comparison with the readout of the data logger.

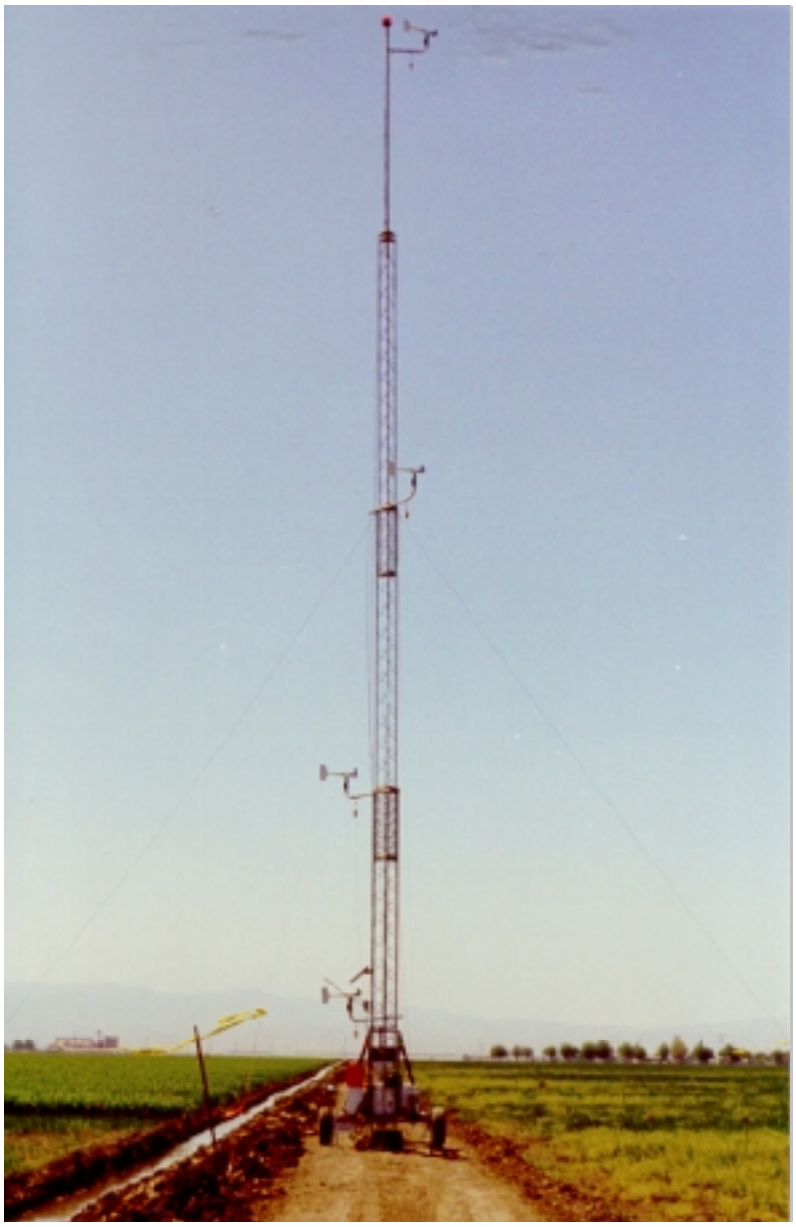

Figure 2-8. Meteorological tower used for the passive flux and active sampling at California State University, Fresno, sites.

The wind direction sensor was aligned with true north using a compass mounted on a tripod. Response was verified by comparing the data logger output with compass measurements while the sensor was held at the four cardinal directions. The temperature sensor was calibrated by immersing the sensing element in water in close proximity to a NIST thermometer. Three nominal temperature were used: 0, 20, and 40 ºC.

All pertinent meteorological data employed in determining the active samples are reported in

Table 4-1, which lists the comparison between the active samples with those of the passive flux sampler.

2.8 Active Sampling

Two methods of active sampling were employed during the project. The first used the same phosphoric acid denuders as utilized for the passive flux samplers but configured in an active sampler. This was only used for the Citrus Grove part of the program (see Section 2.5.1). The second used filter paper impregnated with citric acid and the sampler assembly (Figure 2-9.) NH_3 forms ammonium citrate and stays on the filter paper; subsequent lab analysis determines micrograms of NH_3 on the filter paper**.** For the last four sites, filter pack only samples were taken. Analysis of the filter pack samples was conducted at the lab facilities of Fresno State University.

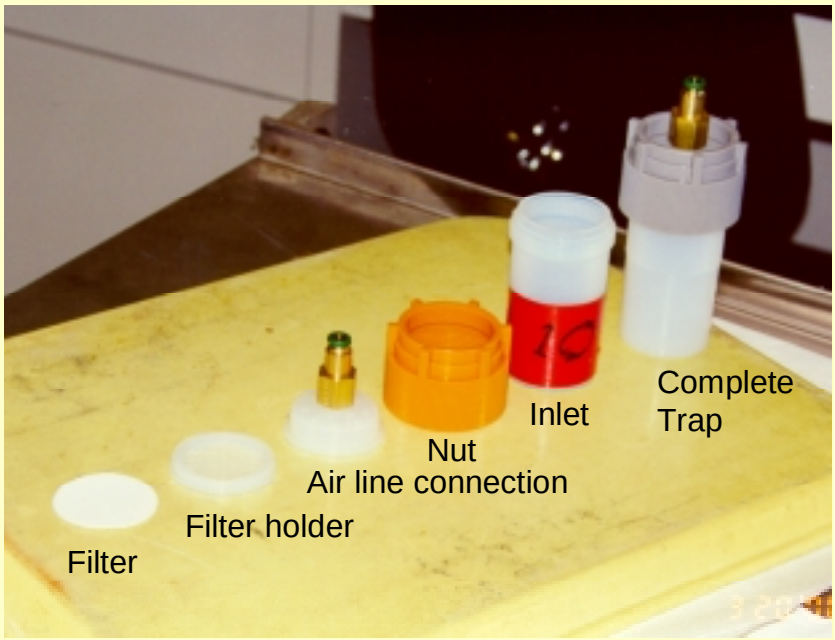

Figure 2-9. Filter pack active sampler assembly.

For the duration of the study all sample pumps underwent verification of their respective flow rate with the active samplers attached. For each sample period, the flow rate was adjusted with a dedicated in-line sampler rotameter to 9 L/min. A single calibration rotameter was used to

calibrate the in-line flow indicator by placing it at the inlet while sampling with substrates loaded into the holder. The calibration rotameter in turn was calibrated with a dry test meter (Singer model DTM-115) that has a primary calibration traceable to the NIST. This is a multi-point calibration that used five nominal flow rates (2, 4, 6, 8, 10 L/min). The flows were determined over a 1-minute nominal period timed with a handheld digital stopwatch. Flow rates were converted to standard conditions of temperature and pressure and a calibration equation obtained from a linear regression of the data. Temperature was determined with a thermometer traceable to NIST. Site pressure was calculated from the altimeter setting obtained at the Riverside and Fresno airports and adjusted for differences in elevation using a topographic map. Appendix B shows an example of the form used for calibration during the field program.

Figure 2-10. Citrate impregnated filter.

Citrate impregnated filters (Figure 2-10) were placed face-down on the meteorological tower at a location approximately near the center of the passive flux sampler but at least 8-10 cm lower so as to not bias the wind flow through the passive sampler. Figure 2-11 shows a complete experimental assembly with two passive flux samplers collocated and the active filter pack sampler as well as an active denuder sampler all at one elevation. Restrictions in the number of samplers available required that the last four sites had only passive flux samples and filter pack

samples for comparison. This, however, was provided at all elevations and led more than 30 direct comparisons.

Figure 2-11. Complete experimental assembly with two passive flux samplers collocated and the active filter pack sampler as well as an active denuder sampler all at one elevation.

2.9 Sample Identification

Considering the number of samples that were required for the project, a specific method for sample identification was created so as to minimize risk that the samples would be improperly allocated when analyzed. Pre-printed forms were used to tabulate pertinent sampling data. This includes denuder number, sampler ID and location, beginning and end indicated flow rates, date, time, and identification of the experimenter performing the substrate loading and unloading. A sample is listed below for the pig operation where three independent locations were simultaneously sampled.

Using the sample identification ***CAXYZOHHDDMMYY***

Where:

CA = Project Identification, CARB Ammonia

X = Sample pole number (1-9)

Y = Elevation level (1-9)

Z = Direction (N, S, E, W)

O = Orientation (F= front, B = back)

HH = Hour in which collection was started, 24 hour local time

DD = Day of the month

MM = Month

YY = Year

For the pig operation the following parameters were used:

- Sample pole 1 is a 20 m tower located 50 m downwind.
- Sample pole 2 is a 5 m tower located 125 m downwind.
- Sample pole 3 is a 1 m pole located upwind.
- Elevation level 1 is 1 m.
- Elevation level 2 is 2 m.
- Elevation level 3 is 5 m.
- Elevation level 4 is 10 m.

So for example ***CA11NF12101200*** is CARB Ammonia Study (***CA***) at the pig farm tower (***1***), 1-meter elevation (***1***), North Front Denuder (***NF***), started at 12:00 hrs (***12***) on December 10th (***1012***), 2000 (***00***).

Substrates were stored before sampling in Petri dishes prior to loading in the filter holder. After sampling, the substrates were transferred from the holder to capped polypropylene cuvettes for storage. Both Petri dished and cuvettes were stored in sealed polyethylene bags containing paper towels treated with a phosphoric acid solution. A copy of the sampling form accompanied the sample and each movement and change in custody was noted on this form. We believe that none of the samples were mislabeled during field measurements and subsequent handling procedures for analysis were restricted in a way to ensure that each experimental day was analyzed independently. Appendix C contains an example of this form.

3.0 RESULTS

The passive flux sampler results are presented in sections 3.1 to 3.5 respectively for each of the sites investigated. Denuder collection efficiencies were determined by first assuming that the collection efficiency of each individual denuder is identical.

$$E = (1 - L_2/L_1)*100 = \text{Percent Efficiency} \quad (2)$$

where:

L_1 = ion load measured on first denuder in series

L_2 = ion load measured on second denuder in series

Note that this calculation assumes that the collection efficiencies of each denuder remained constant during sampling. Should the collection efficiencies decrease with increased loading, this formula will underestimate collection efficiency. Since the sample period was held to four hours, we were unlikely to reach levels of loading on the denuder where efficiency decreased for that reason. By looking at the highest level of ammonia flux measured, the collocated sample of dairy 2 at 2 m, it is clear that this is the case as denuder efficiency was still greater than 90%. There are at times throughout the data where efficiencies fall below 50%; this is usually for low ammonia flux levels where the effects of diffusion contribute more than the flux through the denuder. To include the effects of diffusion for the passive samples, the horizontal ammonia flux was determined by adding the net amount of ammonium that was collected by each denuder pair (front and back for a single direction) and dividing this sum by the denuder's collection surface area. Knowing the sample time (for most of the data taken during theses experiments the time was approximately 240 min) and the active surface area of the denuder (13.9 cm^{-2}) results in the total flux through the denuder for each of the 4 directions. The strongly biased directions, for example the north and west for the dairy at one meter, show high denuder efficiencies of greater than 90%. The directions opposite to the primary wind direction show much lower efficiencies and clearly have components of diffusion as well as turbulence. The lowest value of ammonia flux, which for this data set occurred for the dairy 5 m from the south, of 1.0 $ng/cm^2/min$, can be used as a reasonable approximation for the diffusion component (D). Over the sampling days the diffusion component, determined this way, had a variance of 1.0 $ng/cm^2/min$. Therefore, the total

net ammonia flux is the sum of the fluxes from the four directions (*i*) minus the diffusion component in each.

$$\Phi_{NH3} = \Sigma(\Phi_{NH3})_i\text{-}4D \qquad (3)$$

3.1 Citrus Grove

The first measurements taken with the passive flux sampler were conducted at the citrus grove. Upwind samples were collected west of the grove, downwind to the east. The upwind and downwind locations were on each end of the grove, 230 m apart. The wind was blowing almost directly from the west during the sampling period. The results for the passive sampling are summarized in Table 3-1. For the passive samples facing the west, the efficiency was approximately 90%. This is in good agreement with the active sampling conducted here and with previous active denuder sampling. For this one application, comparison was made with the passive denuder and active sampling with similar denuders. Subsequent testing compared passive denuder samples with citrus acid coated filter packs. Table 3-2 lists the results from the active denuder samples. All samples are consistent with the direction of the ammonia source. As expected, the fluxes for the downwind samplers from the east were all lower than the other three directions. Both the south-facing and the north-facing denuders are expected to collect some ammonia flux due to the variability of the wind direction. Since no component of wind would be from the east, this eastern "flux" most likely is a measure of diffusion of ammonia to the denuder and subtracted from the other three directions. The other three directions were then added together to determine the total ammonia flux at each elevation. These values are shown in the sum of the total ammonia flux column.

Figure 3-1 shows a plot of NH_3 flux versus wind direction. We observe the strong bias of the flux toward the west, the direction of the citrus grove in relation to the sample location. Notice that the peak flux occurred at 10 m above the ground. The active sampling data in Table 3-2 clearly show the expected decreasing concentrations with elevation.

Table 3-1. Citrus grove passive sampling results.

Sample ID Field	Total Flux Through Denuder ng/cm^2/min	Denu-der effici-ency	Total Flux Through Denuder ng/cm^2/min	Total NH_3 Flux
South Front	5.9	84%	7.0	3.4
South Back	1.1			
North Front	5.9	75%	7.8	4.2
North Back	1.9			
West Front	19.4	95%	20.3	16.7
West Back	0.9			
East Front	1.8	51%	3.6	0.0
East Back	1.8			
Citrus Grove 1m Downwind				24.4

Sample ID Field	Total Flux Through Denuder ng/cm^2/min	Denu-der effici-ency	Total Flux Through Denuder ng/cm^2/min	Total NH_3 Flux
South Front	8.8	84%	10.5	6.9
South Back	1.7			
North Front	4.7	69%	6.8	3.2
North Back	2.1			
West Front	34.2	86%	39.6	36.0
West Back	5.4			
East Front	1.7	41%	4.0	0.4
East Back	2.4			
Citrus Grove 10m Downwind				46.1

South Front	7.3	78%	9.4	5.8
South Back	2.1			
North Front	6.6	82%	8.1	4.5
North Back	1.5			
West Front	20.5	88%	23.3	19.7
West Back	2.8			
East Front	1.8	45%	4.1	0.5
East Back	2.2			
Cirus Grove 4m Downwind				30.1

South Front	8.8	74%	11.9	8.3
South Back	3.2			
North Front	8.8	71%	12.4	8.8
North Back	3.6			
West Front	28.5	89%	31.8	28.2
West Back	3.4			
East Front	2.0	42%	4.8	1.2
East Back	2.8			
Citrus Grove 13m Downwind				45.3

South Front	10.0	83%	12.1	8.5
South Back	2.1			
North Front	3.9	65%	6.0	2.4
North Back	2.1			
West Front	28.6	90%	31.6	28.0
West Back	3.1			
East Front	2.8	70%	3.9	0.3
East Back	1.2			
Citrus Grove 7m Downwind				38.9

South Front	1.9	53%	3.6	0.0
South Back	1.7			
North Front	2.1	54%	3.8	0.2
North Back	1.7			
West Front	2.4	71%	3.4	-0.2
West Back	1.0			
East Front	1.7	56%	3.0	-0.6
East Back	1.3			
Citrus Grove 1m Upwind				0.0

Table 3-2. Citrus grove active sampling results.

Sample ID Field	Concentration ugNH3/m3	Denuder efficiency %	Effective Wind Speed m/sec	Total Ammonia Flux ng/cm2/min
2m, Downwind Front Denuder	79.9	91	1.18	618.6
2m, Downwind Back Denuder	7.4			
7m, Downwind Front Denuder	45.0	91	1.43	425.3
7m, Downwind Back Denuder	4.6			
13m, Downwind Front Denuder	28.6	88	1.56	304.3
13m, Downwind Back Denuder	3.9			
2m, Upwind Front denuder	13.1	80	1.18	115.1
2m, Upwind Back Denuder	3.2			

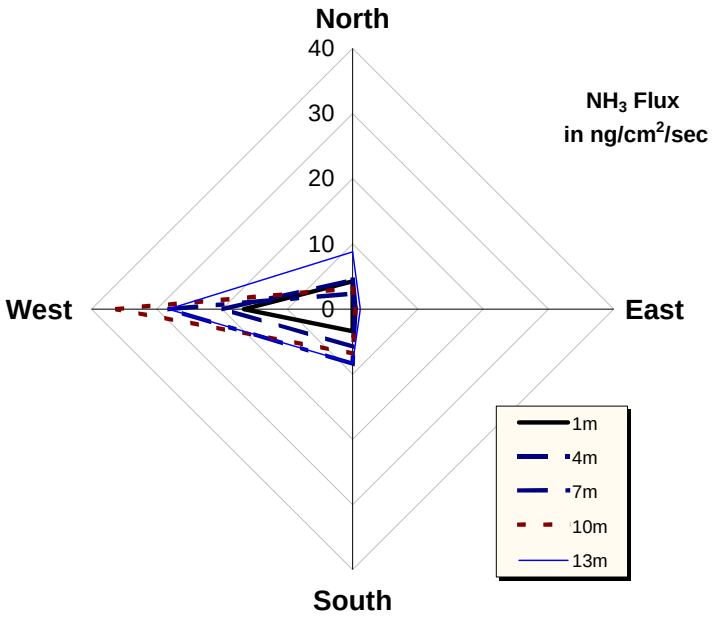

Figure 3-1. Spider plot showing the ammonia flux from the citrus grove versus wind direction.

Figure 3-2 shows the flux is increasing with elevation until the 10 m mark and then decreases at the 13 m. The ammonia flux peaked at 10 m, most likely due to the increased wind speed compared with lower elevations. The highest elevation was still in the ammonia plume since both the flux and concentrations were higher than the upwind locations. Although the top of the ammonia plume could not be determined, the data clearly indicate that these measurements can be used to estimate the flux of ammonia from an area source. Since the top of the plume was not determined in this case, the emission rate can only be estimated. This can be accomplished by modeling the existing data and extrapolating to the full extent of the plume and is presented in Section 4.4. When comparing the active sampling denuder results with those of the passive flux sampler, the passive flux sampler underestimates the flux by 6.7 times at the 13 m elevation, 10.9 times at the 7 m elevation, and approximately 25 times over the 1-2 m elevation range. This is primarily from the flow abatement through the passive flux sampler; the difference is likely due to effects on the flow through the passive flux denuder assembly by having larger swings in wind direction at the higher levels.

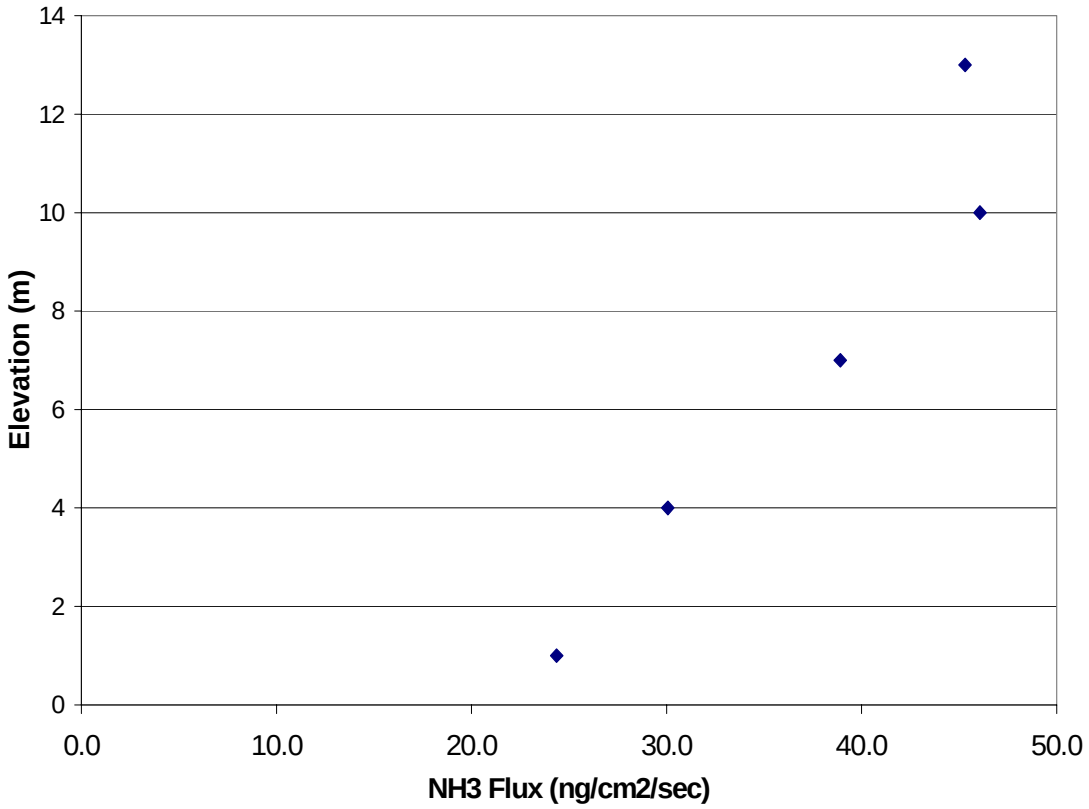

Figure 3-2. Ammonia flux elevation profile from the citrus grove.

3.2 Dairy Farm

The samples from the dairy farm were analyzed for ammonia. Upwind samples were collected northwest of the dairy farm, downwind ones to the southeast (Figure 3-3). The upwind and downwind locations were on each end of the dairy farm. The downwind sample was approximately 50 meters from the edge of the dairy operation in line with C on the layout.

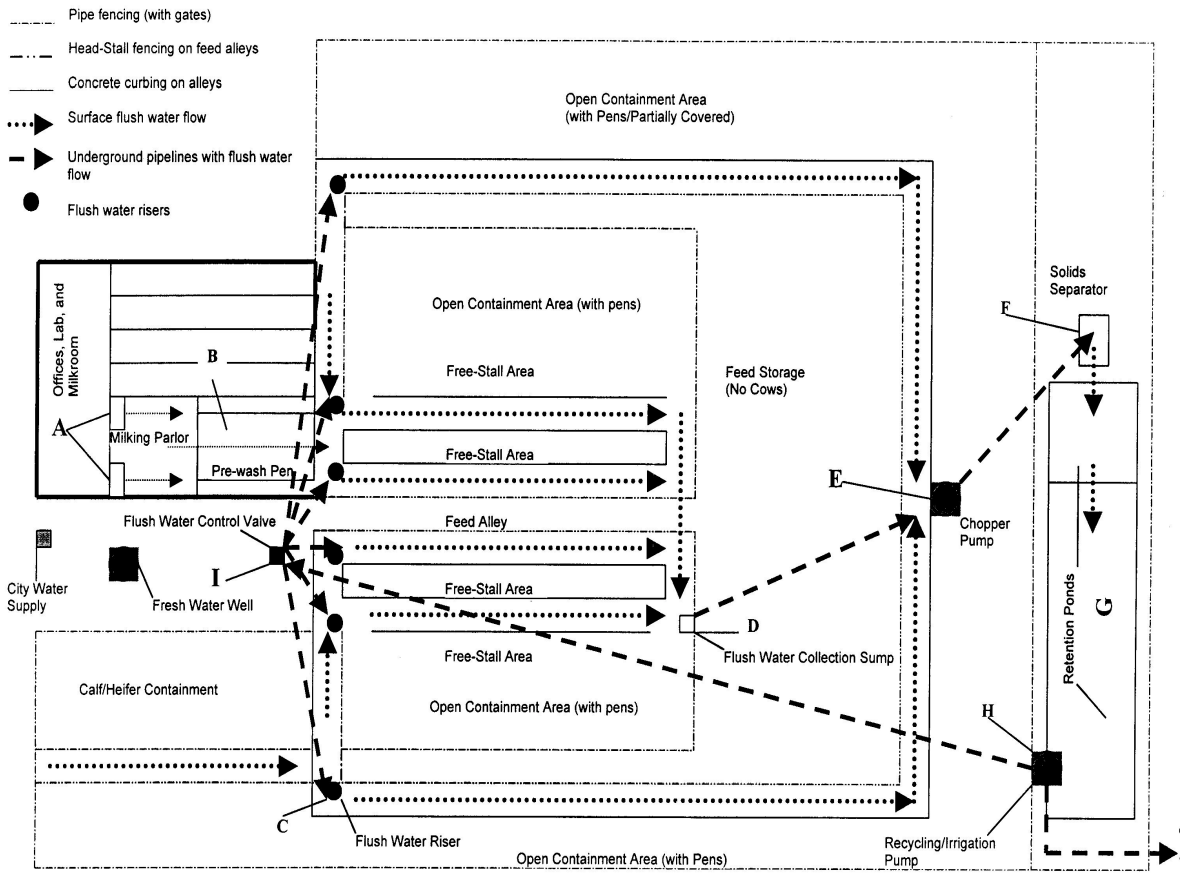

Figure 3-3. Plot plan for dairy site. Drawing is not to scale; the width of the dairy is approximately 400 m. The letter G on the layout marks the dairy lagoon.

We assumed by locating at the edge that we could isolate effects from the dairy lagoon, which was located due north. The upwind sample was almost 100 m northwest of the dairy farm. The dairy farm was located northwest of the sampling tower, and winds came from the northwest with average speeds of 1.5 to 2.3 m/s. The average directions were between 295 to 305 degrees. The dairy farm was measured over two separate days.

The results for the passive sampling are summarized in Table 3-3 for day 1 and Table 3-4 for day 2. For the passive samples, the flux levels appear to be relatively evenly split between the north and the west. In these two directions denuder efficiencies are nominally greater than 90%. All samples are consistent with the direction of the ammonia source. As expected, the fluxes for the downwind samplers from the south and east were all lower than from the other two directions. Both the south-facing and the east-facing denuders are expected to collect some ammonia flux due to the variability of the wind direction and diffusion. Since the lowest component of wind came from the southern direction at 5 m, this southern "flux" was used to estimate the diffusion

component of ammonia to the denuder and subtracted from the other three directions for all heights. This was used for the next days sampling as well since the tower location did not change. The other three directions were then added together to determine the total ammonia flux at each elevation. These values are shown in the sum of the Total Ammonia Flux column.

An extra sample was taken an additional 100 m downwind at an elevation of 2 m. The total flux at this position was less than 5% of the flux measured at the 50 m location at the same height. This shows that the NH_3 disperses quickly and was just slightly higher than the upwind sample, which was 0.9 ng/cm^2/min. Figures 3-4 and 3-5 are spider type plots showing the contribution to the total ammonia flux from each direction for the two sampling periods at the dairy farm. We observe that with similar wind patterns as encountered for the four-hour sampling period that the plots show a strong northwest bias at similar height levels.

The plots also show that there is almost equal contribution to the total flux from the north and west denuders. There is a markedly strong gradient to the ground as the net flux contribution from the 5 m elevation is significantly lower. Since the wind speed, direction and temperature were fairly consistent for the two days, the close agreement of the two data sets indicate that emission rates from the dairy are fairly consistent under similar climatic conditions.

The dairy set had two collocated passive flux samplers at 2 m. They showed close agreement and are further discussed in Section 4.1. Comparison between the passive flux data with that of the active filter pack data is discussed in Section 4.2. As indicated in Figure 3-6, the maximum flux levels occur nearer the surface on both days. The net flux was reduced at the 5 m level by approximately a factor of 2 and 3 respectively for the two days of sampling. Although the 5 m elevation sampler did not capture the height of the plume, the significant drop in net flux at that level permits a reasonable approximation of the emission rate with only measurement at three elevations.

Table 3-3. Dairy farm day 1 passive sampler results. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonia Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
4NF	CA21NF12021000	111.6	94%	28.6	27.5
4NB	CA21NB12021000	7.4			
4SF	CA21SF12021000	10.1	57%	4.2	3.2
4SB	CA21SB12021000	7.6			
4EF	CA21EF12021000	4.1	38%	2.6	1.6
4EB	CA21EB12021000	6.7			
4WF	CA21WF12021000	116.9	93%	30.2	29.2
4WB	CA21WB12021000	8.8			
	DAIRY 1 METER				61.5
5NF	CA22NF12021000	98.6	92%	25.6	24.6
5NB	CA22NB12021000	8.2			
5SF	CA22SF12021000	10.2	52%	4.7	3.7
5SB	CA22SB12021000	9.5			
5EF	CA22EF12021000	3.8	32%	2.9	1.8
5EB	CA22EB12021000	8.1			
5WF	CA22WF12021000	106.9	93%	27.5	26.5
5WB	CA22WB12021000	7.7			
	DAIRY 2 METER				56.6
7NF	CA23NF12021000	56.2	100%	13.5	12.4
7NB	CA23NB12021000	-0.1			
7SF	CA23SF12021000	3.0	69%	1.0	0.0
7SB	CA23SB12021000	1.3			
7EF	CA23EF12021000	22.7	78%	7.0	5.9
7EB	CA23EB12021000	6.3			
7WF	CA23WF12021000	87.2	99%	21.1	20.1
7WB	CA23WB12021000	0.8			
	DAIRY 5 METER				38.5
6NF	CA32NF12021000	112.6	94%	28.6	27.6
6NB	CA32NB12021000	6.6			
6SF	CA32SF12021000	7.5	52%	3.4	2.4
6SB	CA32SB12021000	6.9			
6EF	CA32EF12021000	6.3	36%	4.2	3.2
6EB	CA32EB12021000	11.3			
6WF	CA32WF12021000	130.5	93%	33.7	32.7
6WB	CA32WB12021000	9.8			
DAIRY(Co-located) 2 METER					65.8
9NF	CA51NF12021000	6.4	98%	1.6	1.6
9NB	CA51NB12021000	0.1			
9SF	CA51SF12021000	-0.6	970%	0.0	0.0
9SB	CA51SB12021000	0.5			
9EF	CA51EF12021000	1.6	43%	0.9	0.9
9EB	CA51EB12021000	2.2			
9WF	CA51WF12021000	6.2	74%	2.0	2.0
9WB	CA51WB12021000	2.1			
DAIRY 100 METERs DOWNWIND					4.5

Table 3-4. Dairy farm day 2 passive sampler results. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
24NF	CA21NF11031000	153.4	92%	40.1	39.0
24NB	CA21NB11031000	13.4			
24SF	CA21SF11031000	14.2	66%	5.2	4.1
24SB	CA21SB11031000	7.3			
24EF	CA21EF11031000	8.2	47%	4.2	3.2
24EB	CA21EB11031000	9.3			
24WF	CA21WF11031000	143.4	93%	37.0	36.0
24WB	CA21WB11031000	10.8			
	DAIRY 1 METER				82.3
25NF	CA22NF11031000	150.7	91%	40.0	38.9
25NB	CA22NB11031000	15.7			
25SF	CA22SF11031000	13.6	56%	5.9	4.8
25SB	CA22SB11031000	10.9			
25EF	CA22EF11031000	8.6	40%	5.1	4.1
25EB	CA22EB11031000	12.7			
25WF	CA22WF11031000	148.2	93%	38.2	37.2
25WB	CA22WB11031000	11.1			
	DAIRY 2 METER				85.1
26NF	CA23NF11031000	43.0	85%	12.1	11.1
26NB	CA23NB11031000	7.5			
26SF	CA23SF11031000	8.1	53%	3.7	2.6
26SB	CA23SB11031000	7.1			
26EF	CA23EF11031000	11.3	64%	4.2	3.2
26EB	CA23EB11031000	6.3			
26WF	CA23WF11031000	39.8	88%	10.9	9.9
26WB	CA23WB11031000	5.6			
	DAIRY 5 METER				26.8
27NF	CA32NF11031000	165.7	90%	44.4	43.4
27NB	CA32NB11031000	19.3			
27SF	CA32SF11031000	13.8	53%	6.2	5.2
27SB	CA32SB11031000	12.0			
27EF	CA32EF11031000	8.0	38%	5.1	4.1
27EB	CA32EB11031000	13.2			
27WF	CA32WF11031000	162.6	93%	42.1	41.0
27WB	CA32WB11031000	12.5			
	DAIRY(Co-located) 2 METER				93.6
29NF	CA51NF11031000	5.7	96%	1.4	1.4
29NB	CA51NB11031000	0.3			
29SF	CA51SF11031000	0.8	79%	0.3	0.3
29SB	CA51SB11031000	0.2			
29EF	CA51EF11031000	0.6	30%	0.5	0.5
29EB	CA51EB11031000	1.4			
29WF	CA51WF11031000	4.2	89%	1.1	1.1
29WB	CA51WB11031000	0.5			
	DAIRY 100 METERs DOWNWIND				3.3

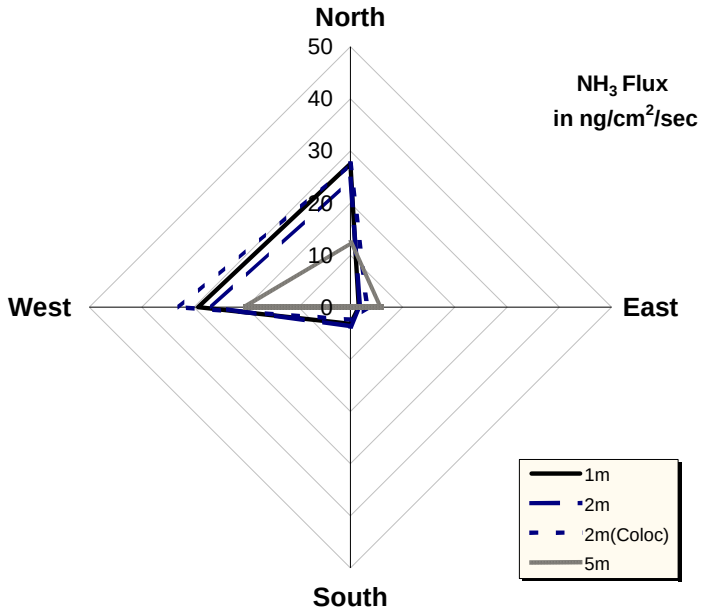

Figure 3-4. Spider plot showing the ammonia flux from the dairy farm versus wind direction on the first day of sampling.

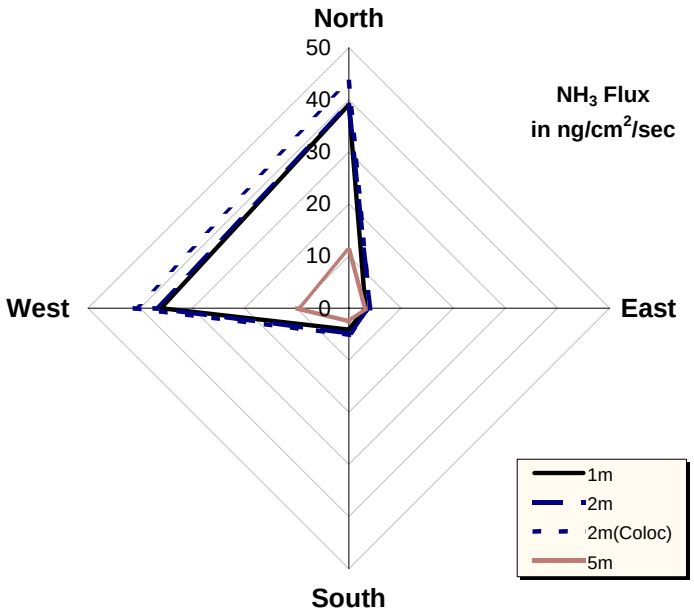

Figure 3-5. Spider plot showing the ammonia flux from the dairy farm versus wind direction on the second day of sampling.

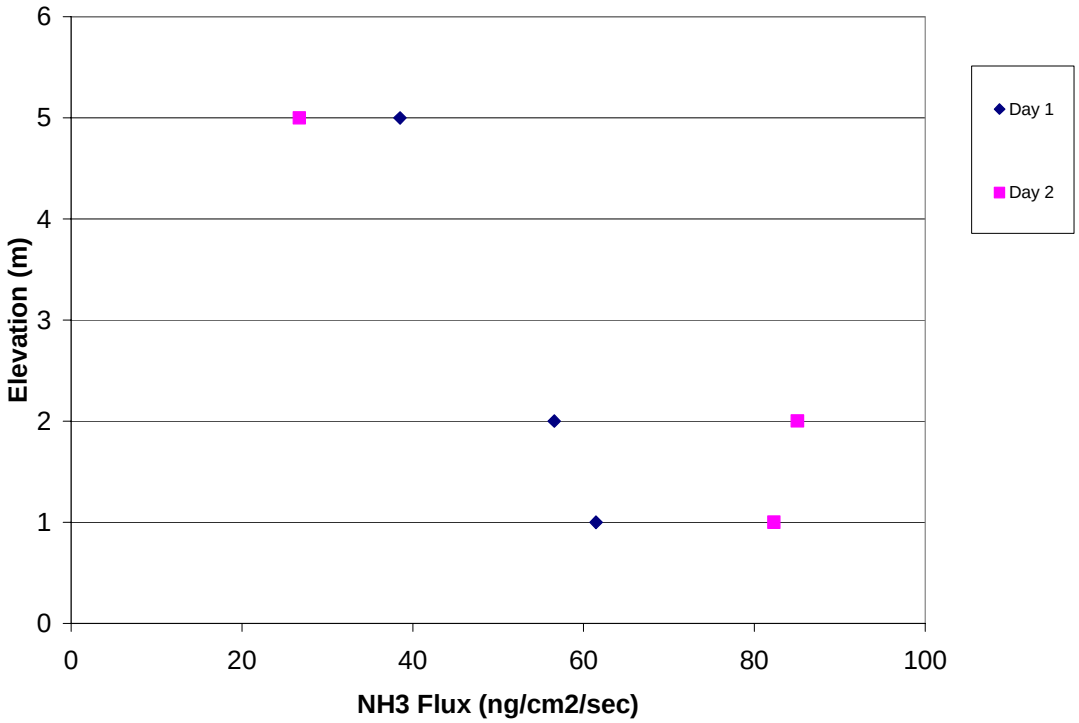

Figure 3-6. Ammonia flux elevation profile from the dairy farm over the two days of sampling.

3.3 Dairy Lagoon

Sampling was conducted for ammonia from the dairy lagoon adjacent to the dairy operation. The samples were taken over a 3-day period before, during, and after acidification of the lagoon. The lagoon was acidified with sulfuric acid. Results are listed in Table 3-5 (pre acidification), Table 3-6 (during acidification) and 3-7 (post acidification). The wind was blowing from the northwest during the sampling period.

The tower was located southeast of the secondary lagoon, but the primary lagoon was located due west of the secondary lagoon and therefore expected to have an increase in the western component of the NH_3 flux. The sampling tower contained active filter pack as well as meteorological wind speed and direction sensors at levels up to 10 m. The passive flux samplers were only installed up to the 5 m level due to the proximity of the tower to the emission source.

Figure 3.7. Primary and secondary lagoons, viewed from the east. Sampling occurred near the location of the drainage pump, which is to the right of the secondary lagoon.

Table 3-5. Dairy lagoon pre-acidification passive sampler results. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
1NF	CA11NF12021000	66.2	91%	17.5	14.8
1NB	CA11NB12021000	6.8			
1SF	CA11SF12021000	22.4	78%	6.9	4.2
1SB	CA11SB12021000	6.1			
1EF	CA11EF12021000	6.8	45%	3.6	0.9
1EB	CA11EB12021000	8.1			
1WF	CA11WF12021000	138.6	94%	35.3	32.6
1WB	CA11WB12021000	8.5			
	LAGOON 1 METER				52.5
2NF	CA12NF12021000	81.7	95%	20.7	18.0
2NB	CA12NB12021000	4.6			
2SF	CA12SF12021000	11.0	60%	4.4	1.7
2SB	CA12SB12021000	7.3			
2EF	CA12EF12021000	4.3	38%	2.7	0.0
2EB	CA12EB12021000	6.9			
2WF	CA12WF12021000	169.4	97%	42.1	39.4
2WB	CA12WB12021000	5.7			
	LAGOON 2 METER				59.1
3NF	CA13NF12021000	37.2	68%	13.2	10.5
3NB	CA13NB12021000	17.8			
3SF	CA13SF12021000	30.5	85%	8.6	5.9
3SB	CA13SB12021000	5.2			
3EF	CA13EF12021000	14.2	40%	8.5	5.8
3EB	CA13EB12021000	21.1			
3WF	CA13WF12021000	79.0	90%	21.2	18.5
3WB	CA13WB12021000	9.1			
	LAGOON 5 METER				40.7
8NF	CA41NF12021000	0.0	-1%	-0.2	
8NB	CA41NB12021000	-1.0			
8SF	CA41SF12021000	2.2	76%	0.7	
8SB	CA41SB12021000	0.7			
8EF	CA41EF12021000	0.2	24%	0.2	
8EB	CA41EB12021000	0.6			
8WF	CA41WF12021000	1.7	160%	0.3	
8WB	CA41WB12021000	-0.7			
	LAGOON UPWIND				0.9

Table 3-6. Dairy lagoon during acidification passive sampler results. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
21NF	CA11NF11031000	93.9	92%	24.5	21.8
21NB	CA11NB11031000	8.1			
21SF	CA11SF11031000	14.1	77%	4.4	1.7
21SB	CA11SB11031000	4.2			
21EF	CA11EF11031000	7.9	42%	4.5	1.8
21EB	CA11EB11031000	10.9			
21WF	CA11WF11031000	169.0	85%	47.6	44.9
21WB	CA11WB11031000	29.0			
	LAGOON 1 METER	337.2			70.2
22NF	CA12NF11031000	91.1	91%	24.1	21.4
22NB	CA12NB11031000	9.2			
22SF	CA12SF11031000	14.2	68%	5.0	2.3
22SB	CA12SB11031000	6.8			
22EF	CA12EF11031000	4.8	35%	3.3	0.6
22EB	CA12EB11031000	9.0			
22WF	CA12WF11031000	159.2	92%	41.5	38.8
22WB	CA12WB11031000	13.7			
	LAGOON 2 METER	307.9			63.2
23NF	CA13NF11031000	60.5	86%	16.9	14.2
23NB	CA13NB11031000	9.7			
23SF	CA13SF11031000	14.5	60%	5.9	3.2
23SB	CA13SB11031000	9.9			
23EF	CA13EF11031000	13.9	48%	6.9	4.2
23EB	CA13EB11031000	14.8			
23WF	CA13WF11031000	83.5	86%	23.4	20.8
23WB	CA13WB11031000	14.1			
	LAGOON 5 METER	220.9			42.3
28NF	CA41NF11031000	5.6	110%	1.2	
28NB	CA41NB11031000	-0.5			
28SF	CA41SF11031000	-0.2	39%	-0.2	
28SB	CA41SB11031000	-0.4			
28EF	CA41EF11031000	-0.5	-94%	0.1	
28EB	CA41EB11031000	1.1			
28WF	CA41WF11031000	7.4	104%	1.7	
28WB	CA41WB11031000	-0.3			
	LAGOON UPWIND	12.1			2.9

Table 3-7. Dairy lagoon post-acidification passive sampler results. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
31NF	CA11NF11041000	41.0	84%	11.6	9.0
31NB	CA11NB11041000	7.5			
31SF	CA11SF11041000	8.1	53%	3.7	1.0
31SB	CA11SB11041000	7.1			
31EF	CA11EF11041000	8.8	51%	4.1	1.4
31EB	CA11EB11041000	8.3			
31WF	CA11WF11041000	38.3	87%	10.5	7.8
31WB	CA11WB11041000	5.6			
	LAGOON 1 METER				19.2
32NF	CA12NF11041000	22.9	73%	7.5	4.8
32NB	CA12NB11041000	8.4			
32SF	CA12SF11041000	13.6	66%	5.0	2.3
32SB	CA12SB11041000	7.1			
32EF	CA12EF11041000	7.3	45%	3.9	1.2
32EB	CA12EB11041000	9.0			
32WF	CA12WF11041000	33.4	85%	9.5	6.8
32WB	CA12WB11041000	6.0			
	LAGOON 2 METER				15.1
33NF	CA13NF11041000	10.1	62%	3.9	1.2
33NB	CA13NB11041000	6.3			
33SF	CA13SF11041000	14.5	64%	5.5	2.8
33SB	CA13SB11041000	8.3			
33EF	CA13EF11041000	6.6	44%	3.6	0.9
33EB	CA13EB11041000	8.3			
33WF	CA13WF11041000	26.1	79%	7.9	5.3
33WB	CA13WB11041000	7.0			
	LAGOON 5 METER				10.2
38NF	CA41NF11041000	4.0	52%	1.8	
38NB	CA41NB11041000	3.7			
38SF	CA41SF11041000	5.6	70%	1.9	
38SB	CA41SB11041000	2.4			
38EF	CA41EF11041000	15.2	85%	4.3	
38EB	CA41EB11041000	2.7			
38WF	CA41WF11041000	8.4	82%	2.5	
38WB	CA41WB11041000	1.9			
	LAGOON UPWIND	43.9			10.5

A northwest bias of the individual denuders is observed (Figures 3-8 and 3-9). As expected the stronger western component, due to the location of the tower and geometry of this particular dairy lagoon, is also observed, specifically at the lower heights, 1 and 2 m. Comparing Figures 3-8 and 3-10, pre- and post-acidification spider plots of the net ammonia flux, indicates that the net flux has been abated quite significantly by the acidification process. Before the addition of any acid, the average pH in the primary lagoon was 7.5. It dropped to 6.3 on the day following the addition of approximately 1500 gallons of concentrated sulfuric acid. Overall, there was a decrease in the ammonia fluxes from the lagoon during the experiment.

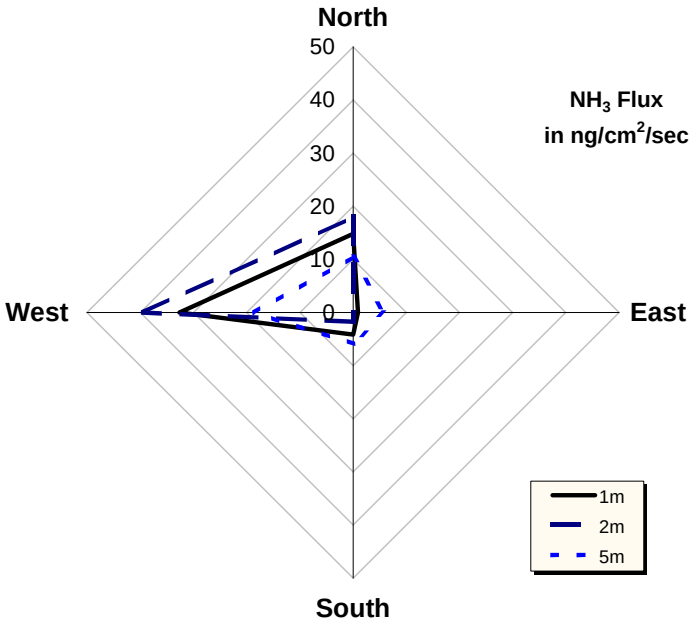

Figure 3-8. Spider plot showing the ammonia flux from the dairy lagoon versus wind direction prior to acidification.

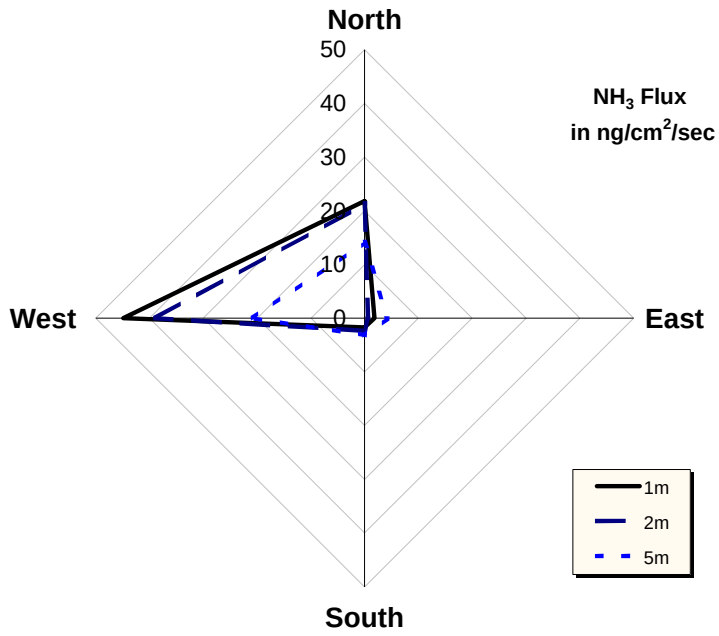

Figure 3-9. Spider plot showing the ammonia flux from the dairy lagoon versus wind direction during acidification.

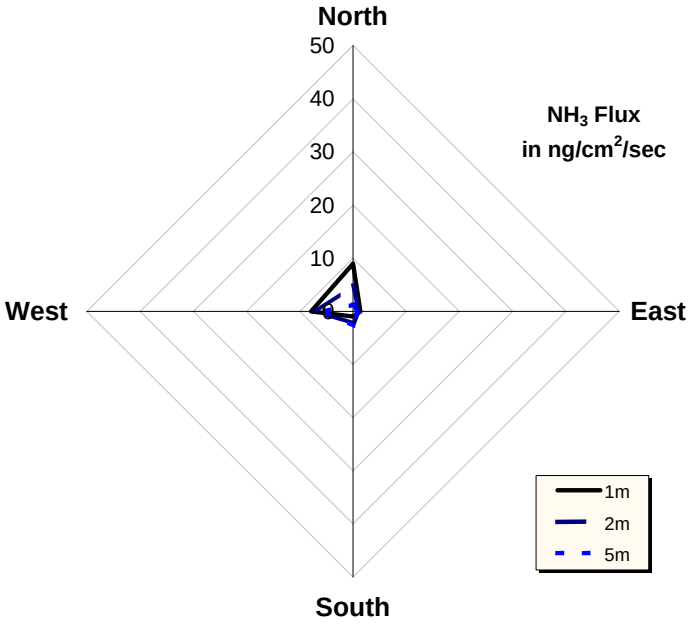

Figure 3-10. Spider plot showing the ammonia flux from the dairy lagoon versus wind direction after acidification.

This is consistent with ammonia emission-pH trends reported in the literature (Zhang et al., 1997). A pH of greater than 7.5 in the lagoon favors NH_3 volatilization. It has also been reported that acidification of cattle slurry can reduce NH_3 emission rates. For example, the relatively highest NH_3 flux observed at the 5 m location during the acidification was probably influenced by the fact that the highest average wind speed was also recorded there. Following the acid injection, the lagoon was aerated for approximately two hours. The primary purpose for the aeration was to maintain a slightly aerobic layer. The aerobic surface was expected to control the odors associated with gases such as ammonia and hydrogen sulfide produced at the bottom of the anaerobic lagoon.

Figure 3-11 shows the 1 m passive flux sampler location. We expected to see higher levels of NH_3 flux closer to the surface because of the sampling tower's proximity to the lagoon.

Figure 3-11. Dairy lagoon showing 1 m sampling location.

This is confirmed in the plot showing the ammonia flux profile for the three sampling days (Figure 3-12). During the first two days of sampling (pre-acidification and during acidification), the net flux is reduced by a factor of approximately 1.5 from the 2 m to 5 m elevations. There appears to be a higher source of ammonia closer to the surface during the acidification process that may have been due to the large bubble formation observed on the surface of the lagoon. The post-acidification profile also shows a consistent drop of about 1.5 from the 2 to 5 m elevation but at much reduced levels.

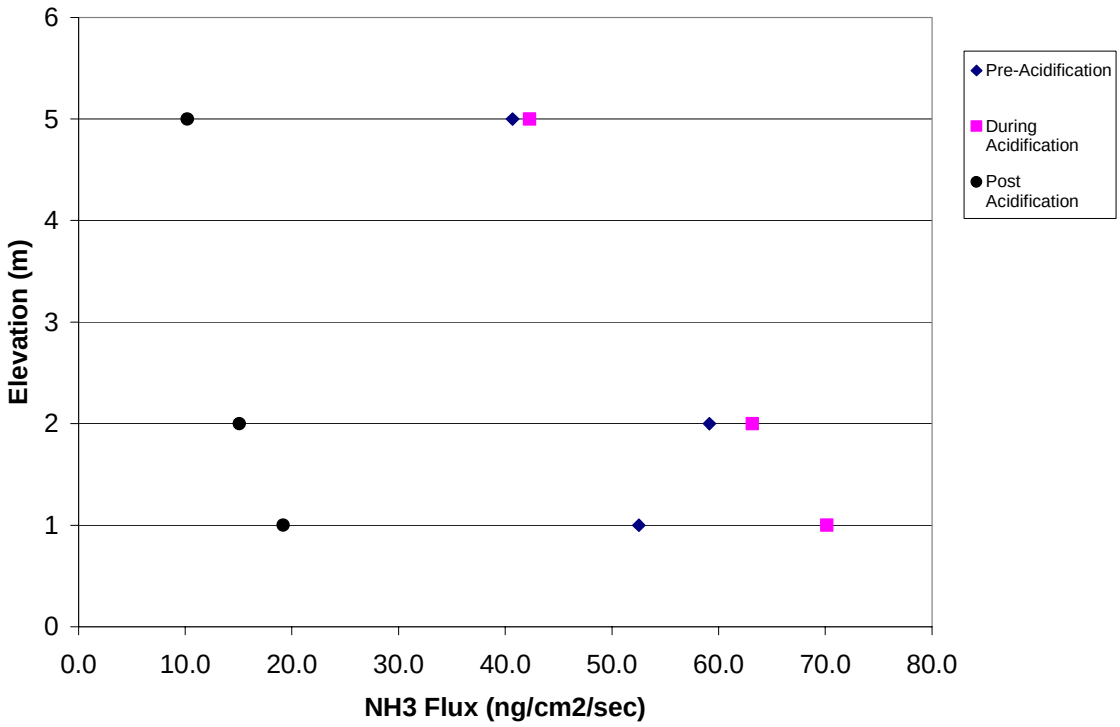

Figure 3-12. Ammonia flux profile for the three sampling days at the dairy lagoon.

3.4 Pig Farm

The pig farm is south and west of the dairy operation. The towers were placed at the southern edge of the pig farm to minimize any contribution from the dairy operation. Upwind samples were collected northwest of the pig farm, downwind to the southeast. The upwind and downwind locations were on each end of the pig farm more than 400 m apart. The wind was blowing almost directly from the northwest during the single-day sampling period.

Samples were taken at two distinct locations. The first was at a distance of 50 m from the southern edge of the farm, and the second was an additional 75 m downwind. The goal of setting two towers was to better understand the dispersion of the NH_3 by treating the pig farm as a line source. First we placed the large tower closer to the farm to ensure capturing the top of the plume. Second, we placed the smaller tower downwind to see what happened to the levels of flux at the first three levels up to 5 m. Since the wind was fairly strong that day, 2.5 to 5 m/s, we expected to be able to see a strong drop in the net flux at the second sampling location.

Tables 3-8 and 3-9 list the results from this site. The upwind data are also included on Table 3-9. The net flux measured at the upwind point, 5.9 (ng/cm^2)/min is fairly high and indicates that we may have the results slightly biased high from another ammonia source. Although we could identify the source with certainty, we are confident from the measurements that the reading was not from wind swirling effects. The wind was very consistent during the sampling period.

From the spider plot of the 50 m tower (Figure 3-13), we clearly see that although we have placed the tower close to the farm, we have not captured the top of the plume as flux levels at 10 m have dropped only by 70%. This is confirmed by the active sampling (refer to Table 4-1), in which we observe that the flux as determined by the active sampling has dropped by approximately 60%. This is a significant issue when determining the extent of the heights we need to measure. Although we nominally measured to 10 m for most of the samples here with the concept that we could facilitate measuring at this height relatively easily, future measurements likely would have to place the passive flux sampler at even higher levels to ensure the capture of the top of the plume.

Table 3-8. Pig farm passive sampler results 50 m downwind. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
4NF	CA11NF11121200	97.1	98%	23.8	23.5
4NB	CA11NB11121200	2.2			
4SF	CA11SF11121200	5.7	67%	2.0	1.7
4SB	CA11SB11121200	2.8			
4EF	CA11EF11121200	1.7	38%	1.1	0.8
4EB	CA11EB11121200	2.8			
4WF	CA11WF11121200	62.1	93%	16.0	15.7
4WB	CA11WB11121200	4.6			
	PIG 1 METER				41.7
5NF	CA12NF11121200	70.2	92%	18.3	17.9
5NB	CA12NB11121200	5.8			
5SB	CA12SF11121200	8.6	66%	3.1	2.8
5SF	CA12SB11121200	4.4			
5EF	CA12EF11121200	3.7	42%	2.1	1.8
5EB	CA12EB11121200	5.2			
5WF	CA12WF11121200	56.4	85%	15.9	15.6
5WB	CA12WB11121200	9.8			
	PIG 2 METERS				38.2
6NF	CA11NF11121200	27.6	89%	7.4	7.1
6NB	CA11NB11121200	3.3			
6SF	CA11SF11121200	2.7	44%	1.5	1.2
6SB	CA11SB11121200	3.5			
6EF	CA11EF11121200	1.9	23%	2.0	1.7
6EB	CA11EB11121200	6.4			
6WF	CA11WF11121200	54.3	90%	14.4	14.1
6WB	CA11WB11121200	5.8			
	PIG 5 METERS				24.1
7NF	CA11NF11121200	11.1	75%	3.6	3.2
7NB	CA11NB11121200	3.7			
7SF	CA11SF11121200	4.9	63%	1.9	1.5
7SB	CA11SB11121200	2.8			
7EF	CA11EF11121200	5.1	40%	3.1	2.8
7EB	CA11EB11121200	7.7			
7WF	CA11WF11121200	14.4	64%	5.4	5.1
7WB	CA11WB11121200	8.0			
	PIG 10 METERS				12.6

Table 3-9. Pig farm passive sampler results an additional 75 m downwind from the 50 m downwind sample location. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
1NF	CA21NF11121200	19.7	93%	5.1	4.8
1NB	CA21NB11121200	1.5			
1SF	CA21SF11121200	5.0	64%	1.9	1.6
1SB	CA21SB11121200	2.8			
1EF	CA21EF11121200	1.2	17%	1.7	1.4
1EB	CA21EB11121200	5.9			
1WF	CA21WF11121200	51.0	91%	13.4	13.1
1WB	CA21WB11121200	4.9			
PIG 1 METER 75 METERS DOWNWIND					20.8
2NF	CA22NF11121200	22.0	92%	5.8	5.4
2NB	CA22NB11121200	2.0			
2SF	CA22SF11121200	1.8	40%	1.1	0.7
2SB	CA22SB11121200	2.7			
2EF	CA22EF11121200	1.1	18%	1.4	1.1
2EB	CA22EB11121200	4.9			
2WF	CA22WF11121200	54.8	92%	14.2	13.9
2WB	CA22WB11121200	4.6			
PIG 2 METER 75 METERS DOWNWIND					21.2
3NF	CA23NF11121200	6.3	85%	1.8	1.5
3NB	CA23NB11121200	1.1			
3SF	CA23SF11121200	3.5	78%	1.1	0.8
3SB	CA23SB11121200	1.0			
3EF	CA23EF11121200	0.8	32%	0.6	0.2
3EB	CA23EB11121200	1.6			
3WF	CA23WF11121200	13.9	91%	3.7	3.3
3WB	CA23WB11121200	1.3			
PIG 5 METER 75 METERS DOWNWIND					5.8
8NF	CA51NF11121200	8.9	84%	2.6	2.3
8NB	CA51NB11121200	1.7			
8SF	CA51SF11121200	1.6	42%	0.9	0.6
8SB	CA51SB11121200	2.2			
8EF	CA51EF11121200	0.7	58%	0.3	0.0
8EB	CA51EB11121200	0.5			
8WF	CA51WF11121200	11.8	86%	3.3	3.0
8WB	CA51WB11121200	2.0			
	PIG 1 METER UPWIND				5.9

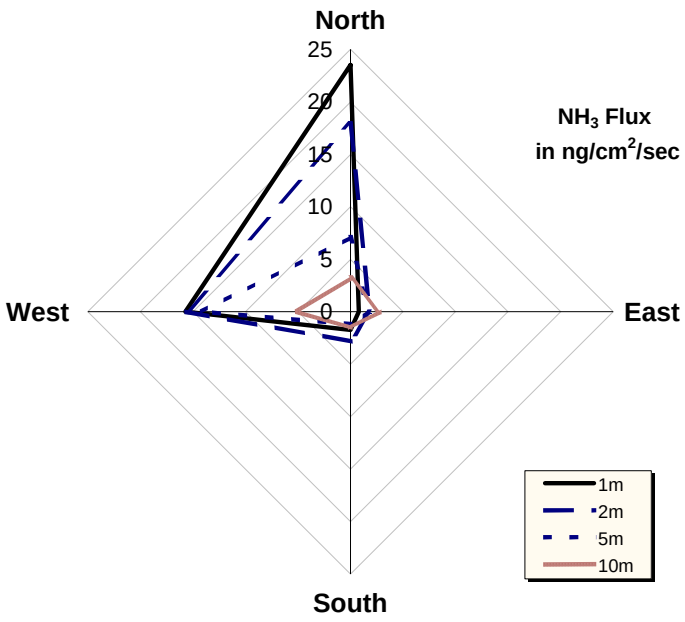

Figure 3-13. Spider plot showing the ammonia flux 50 m southeast from the pig farm versus wind direction.

The results from the second tower shown on Figure 3-14 indicate that there has been a significant drop in the levels of ammonia flux; however, there appears to be a stronger western component when compared to that of the results from the 50 m tower. This likely is due to the influence of a roadway west of the pig farm: Automobile exhaust emissions are known to have significant levels of ammonia (Fraser and Cass, 1998) and may have contributed to the net flux. We did not measure a sample 100 m across from either of the two sampling locations as was done for the dairy farm because of the two sampling towers already involved in the experiment.

The ammonia flux profile in Figure 3-15 appears to indicate a sharp gradient of the flux to the ground at the 50 m location – in fact, the net flux has gone down by almost 75% when compared with the measurement at the 1 and 2 m levels. As expected, the net flux has abated widely from the data taken from the tower at the 125 meter location.

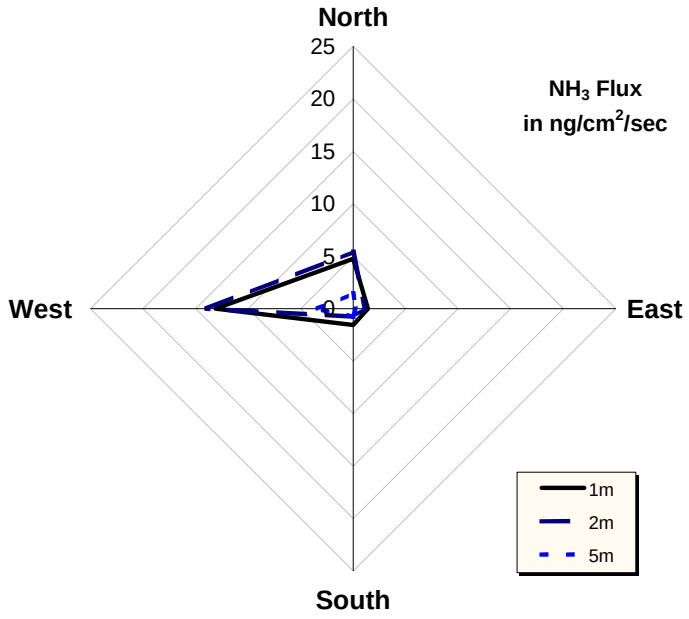

Figure 3-14. Spider plot showing the ammonia flux 125 m southeast from the pig farm versus wind direction.

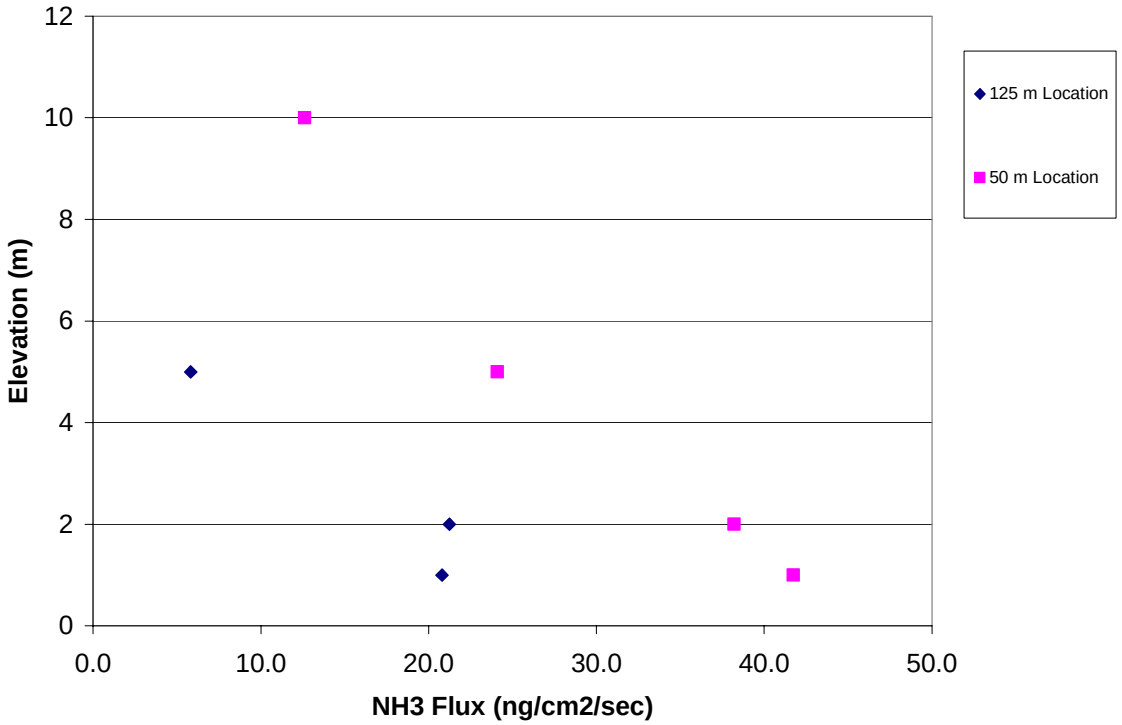

Figure 3-15. Ammonia flux profile southeast from the pig farm versus wind direction.

3.5 Fertilized Field

The samples from the dairy lagoon effluent fertilized field were analyzed for ammonia. The experiment was conducted over two separate days to compare the net flux during the fertilization with the net flux after the field was fertilized. Three locations were selected for sampling. The first was at the location of the fertilized field were the lagoon effluent was first entering. The second was at the field center. The third was to provide one upwind sample. The goal was to see what effects on the net ammonia flux came from this standard fertilization practice.

Figure 3-16 shows the fertilized field the day after being fertilized with lagoon effluent. Notice that there is still a considerable amount of ponding occurring on the surface of the field. The results from the two days of sampling are provided in Tables 3-10 to 3-13. Tables 3-11 and 3-13 are for the field center data; Tables 3-10 and 3-12 show the lagoon effluent entrance data with the upwind sample. All the levels are quite low over the two sampling days except that observed at the field center on day 2. It is not convincing that this method can be used to determine the effects from fertilized fields over a four-hour sampling period. Since the levels are relatively low, it likely requires a longer sampling period. However, because the winds change considerably at this location over the day, the passive flux sampler may not be suitable to measure these types of sources of ammonia. There are some promising indications from this data set in that the passive sampler gave reasonable results on the field center data for the second day, as the winds came from the north and the north component on the spider plot (Figure 3-17) is a factor of 2 higher than any other directional component of the flux over the two day experiment. Notice that the largest component is just above the ground at one meter and there is a significant drop in net ammonia flux at the next level of 2 m.

The levels of flux, although somewhat diffusion-limited, do show a trend over the two days of sampling. When comparing Figures 3-17 and 3-20, we observe that during the fertilizer application the levels are relatively consistent from all directions, but the day after application the bias is to the direction of the field to the west. This is also consistent with what is observed at the field center, Figures 3-18 and 3-21, where very small values in flux were measured during the application but increased to the north and west, the primary direction of the wind. When looking at the ammonia flux profiles for the two days, Figures 3-19 and 3-22, there appears to be a gradient in the net flux to the ground. This is consistent with what would be expected with a

ground-based source and sampling so near to the source. It should be noted, however, that the flux levels are very small and are clearly diffusion-limited.

There appears to be a need to establish at what levels the flux sampler can provide representative data. Although the sampler may not give accurate results for low levels it provides the opportunity to evaluate if the source is a high emitter, in a sense a screening measurement.

Figure 3-16. Fertilized field showing ponding one day after being fertilized with dairy lagoon effluent.

Table 3-10. Lagoon effluent fertilized field at entrance during application. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentratiuon ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
A5NF	CA21NF11131200	10.4	78%	3.2	2.9
A5NB	CA21NB11131200	2.9			
A5SF	CA21SF11131200	17.5	86%	4.9	4.6
A5SB	CA21SB11131200	3.0			
A5EF	CA21EF11131200	6.9	76%	2.2	1.9
A5EB	CA21EB11131200	2.2			
A5WF	CA21WF11131200	8.0	80%	2.4	2.1
A5WB	CA21WB11131200				
	FERTILIZER APPLICATION AT ENTRANCE LOCATION 1 METER HEIGHT				11.4
A6NF	CA22NF11131200	7.1	91%	1.9	1.6
A6NB	CA22NB11131200	0.7			
A6SF	CA22SF11131200	10.9	91%	2.9	2.6
A6SB	CA22SB11131200	1.1			
A6EF	CA22EF11131200	5.3	77%	1.6	1.3
A6EB	CA22EB11131200	1.5			
A6WF	CA22WF11131200	7.0	80%	2.1	1.8
A6WB	CA22WB11131200	1.7			
	FERTILIZER APPLICATION AT ENTRANCE LOCATION 2 METER HEIGHT				7.2
A7NF	CA23NF11131200	6.5	79%	2.0	1.7
A7NB	CA23NB11131200	1.7			
A7SF	CA23SF11131200	11.0	87%	3.0	2.7
A7SB	CA23SB11131200	1.6			
A7EF	CA23EF11131200	5.0	77%	1.6	1.2
A7EB	CA23EB11131200	1.5			
A7WF	CA23WF11131200	5.5	84%	1.6	1.3
A7WB	CA23WB11131200				
	FERTILIZER APPLICATION AT ENTRANCE LOCATION 5 METER HEIGHT				6.9
A8NF	CA51NF11131200	1.3	38%	0.8	0.5
A8NB	CA51NB11131200	2.1			
A8SF	CA51SF11131200	6.2	82%	1.8	1.5
A8SB	CA51SB11131200	1.4			
A8EF	CA51EF11131200	4.4	89%	1.2	0.9
A8EB	CA51EB11131200	0.6			
A8WF	CA51WF11131200	1.2	40%	0.7	0.4
A8WB	CA51WB11131200	1.8			
	FERTILIZER APPLICATION AT OPPOSITE FIELD END 1 METER HEIGHT				3.3

Table 3-11. Lagoon effluent fertilized field at field center during application. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
A1NF	CA11NF11131200	2.7	81%	0.8	0.5
A1NB	CA11NB11131200	0.6			
A1SF	CA11SF11131200	7.1	84%	2.0	1.7
A1SB	CA11SB11131200	1.3			
A1EF	CA11EF11131200	11.2	91%	3.0	2.7
A1EB	CA11EB11131200	1.2			
A1WF	CA11WF11131200	8.3	87%	2.3	2.0
A1WB	CA11WB11131200	1.2			
	FERTILIZER APPLICATION AT FIELD CENTER 1 METER HEIGHT				6.9
A2NF	CA12NF11131200	3.3	79%	1.0	0.7
A2NB	CA12NB11131200	0.9			
A2SF	CA12SF11131200	10.5	91%	2.8	2.4
A2SB	CA12SB11131200	1.0			
A2EF	CA12EF11131200	8.4	86%	2.3	2.0
A2EB	CA12EB11131200	1.4			
A2WF	CA12WF11131200	2.9	56%	1.2	0.9
A2WB	CA12WB11131200	2.2			
	FERTILIZER APPLICATION AT FIELD CENTER 2 METER HEIGHT				6.1
A3NF	CA11NF11131200	3.7	71%	1.3	1.0
A3NB	CA11NB11131200	1.5			
A3SF	CA11SF11131200	10.8	94%	2.8	2.5
A3SB	CA11SB11131200	0.7			
A3EF	CA11EF11131200	3.0	79%	0.9	0.6
A3EB	CA11EB11131200	0.8			
A3WF	CA11WF11131200	4.4	87%	1.2	0.9
A3WB	CA11WB11131200	0.7			
	FERTILIZER APPLICATION AT FIELD CENTER 5 METER HEIGHT				4.9
A4NF	CA11NF11131200	2.7	82%	0.8	0.5
A4NB	CA11NB11131200	0.6			
A4SF	CA11SF11131200	10.1	87%	2.8	2.5
A4SB	CA11SB11131200	1.5			
A4EF	CA11EF11131200	3.4	91%	0.9	0.6
A4EB	CA11EB11131200	0.4			
A4WF	CA11WF11131200	1.7	49%	0.8	0.5
A4WB	CA11WB11131200	1.8			
	FERTILIZER APPLICATION AT FIELD CENTER 10 METER HEIGHT				4.1

Table 3-12. Lagoon effluent fertilized field at entrance the day after application. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
B5NF	CA21NF11141200	14.7	90%	3.9	3.6
B5NB	CA21NB11141200	1.7			
B5SF	CA21SF11141200	7.7	71%	2.6	2.3
B5SB	CA21SB11141200	3.1			
B5EF	CA21EF11141200	2.7	37%	1.8	1.5
B5EB	CA21EB11141200	4.6			
B5WF	CA21WF11141200	19.6	84%	5.6	5.3
B5WB	CA21WB11141200	3.7			
	FERTILIZER APPLICATION AT ENTRANCE LOCATION 1 METER HEIGHT				12.7
B6NF	CA22NF11141200	10.7	91%	2.8	2.5
B6NB	CA22NB11141200	1.1			
B6SF	CA22SF11141200	2.9	84%	0.8	0.5
B6SB	CA22SB11141200	0.5			
B6EF	CA22EF11141200	2.1	44%	1.1	0.8
B6EB	CA22EB11141200	2.6			
B6WF	CA22WF11141200	11.9	86%	3.3	3.0
B6WB	CA22WB11141200	1.9			
	FERTILIZER APPLICATION AT ENTRANCE LOCATION 2 METER HEIGHT				6.9
B7NF	CA23NF11141200	11.8	85%	3.3	3.0
B7NB	CA23NB11141200	2.1			
B7SF	CA23SF11141200	3.5	81%	1.1	0.7
B7SB	CA23SB11141200	0.8			
B7EF	CA23EF11141200	0.9	28%	0.8	0.5
B7EB	CA23EB11141200	2.4			
B7WF	CA23WF11141200	12.4	76%	3.9	3.6
B7WB	CA23WB11141200	4.0			
	FERTILIZER APPLICATION AT ENTRANCE LOCATION 5 METER HEIGHT				7.9
B8NF	CA51NF11141200	13.0	84%	3.7	3.4
B8NB	CA51NB11141200	2.6			
B8SF	CA51SF11141200	4.5	63%	1.7	1.4
B8SB	CA51SB11141200	2.6			
B8EF	CA51EF11141200	6.2	73%	2.1	1.7
B8EB	CA51EB11141200	2.3			
B8WF	CA51WF11141200	11.4	85%	3.2	2.9
B8WB	CA51WB11141200	1.9			
	FERTILIZER APPLICATION AT OPPOSITE FIELD END 1 METER HEIGHT				9.5

Table 3-13. Lagoon effluent fertilized field at center the day after application. High and low efficiencies are the result of the concentrations being near the detection limit.

Sample ID Field	Sample ID Report	Ammonium Concentration ug/denuder	Denuder efficiency	Total Flux Through Denuder ng/cm2/min	Total Ammonia Flux ng/cm2/min
B1NF	CA11NF11141200	37.30	86%	10.47	10.16
B1NB	CA11NB11141200	6.29			
B1SF	CA11SF11141200	2.20	59%	0.89	0.58
B1SB	CA11SB11141200	1.52			
B1EF	CA11EF11141200	2.05	41%	1.19	0.88
B1EB	CA11EB11141200	2.91			
B1WF	CA11WF11141200	14.22	75%	4.55	4.24
B1WB	CA11WB11141200	4.74			
	FERTILIZER APPLICATION AT FIELD CENTER 1 METER HEIGHT				15.86
B2NF	CA12NF11141200	21.61	95%	5.49	5.18
B2NB	CA12NB11141200	1.24			
B2SF	CA12SF11141200	4.57	68%	1.62	1.31
B2SB	CA12SB11141200	2.18			
B2EF	CA12EF11141200	2.46	41%	1.44	1.13
B2EB	CA12EB11141200	3.52			
B2WF	CA12WF11141200	14.31	83%	4.12	3.81
B2WB	CA12WB11141200	2.85			
	FERTILIZER APPLICATION AT FIELD CENTER 2 METER HEIGHT				11.42
B3NF	CA11NF11141200	18.70	93%	4.83	4.52
B3NB	CA11NB11141200	1.42			
B3SF	CA11SF11141200	4.39	80%	1.31	1.00
B3SB	CA11SB11141200	1.08			
B3EF	CA11EF11141200	1.84	39%	1.14	0.83
B3EB	CA11EB11141200	2.90			
B3WF	CA11WF11141200	20.73	92%	5.44	5.13
B3WB	CA11WB11141200	1.92			
	FERTILIZER APPLICATION AT FIELD CENTER 5 METER HEIGHT				11.49
B4NF	CA11NF11141200	10.93	77%	3.42	3.11
B4NB	CA11NB11141200	3.30			
B4SF	CA11SF11141200				
B4SB	CA11SB11141200				
B4EF	CA11EF11141200	3.22	60%	1.29	0.98
B4EB	CA11EB11141200	2.17			
B4WF	CA11WF11141200	17.70	91%	4.67	4.36
B4WB	CA11WB11141200	1.75			
	FERTILIZER APPLICATION AT FIELD CENTER 10 METER HEIGHT				8.45

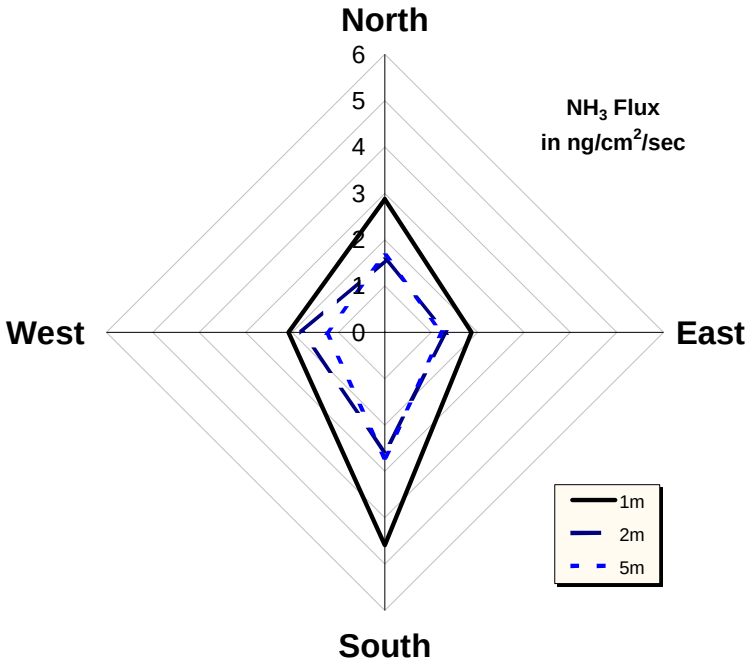

Figure 3-17. Spider plot showing the ammonia flux during the application of fertilizer to a field at the field entrance.

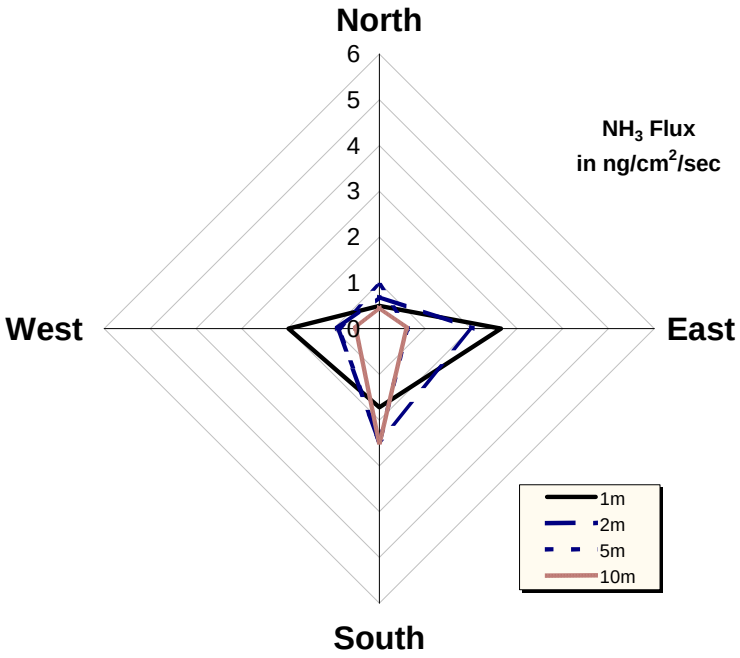

Figure 3-18. Spider plot showing the ammonia flux during the application of fertilizer to a field at the center of the field.

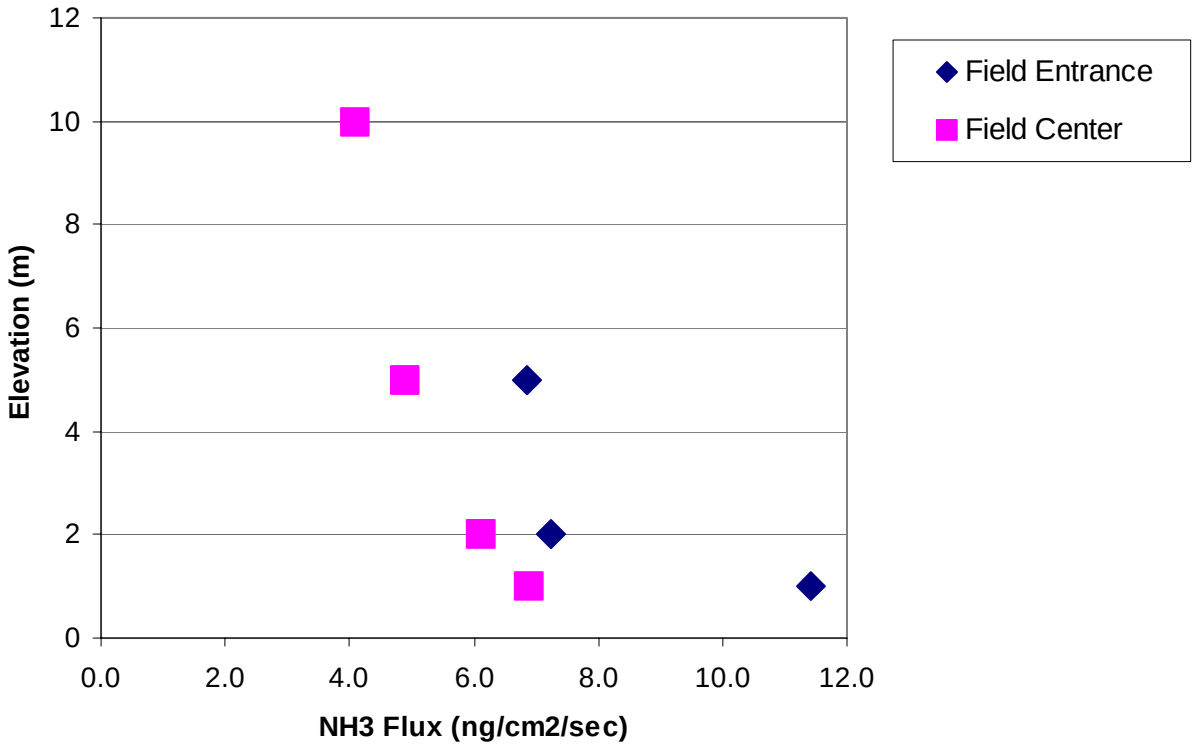

Figure 3-19. Ammonia flux profile during the application of lagoon effluent to a field at the two measured locations.

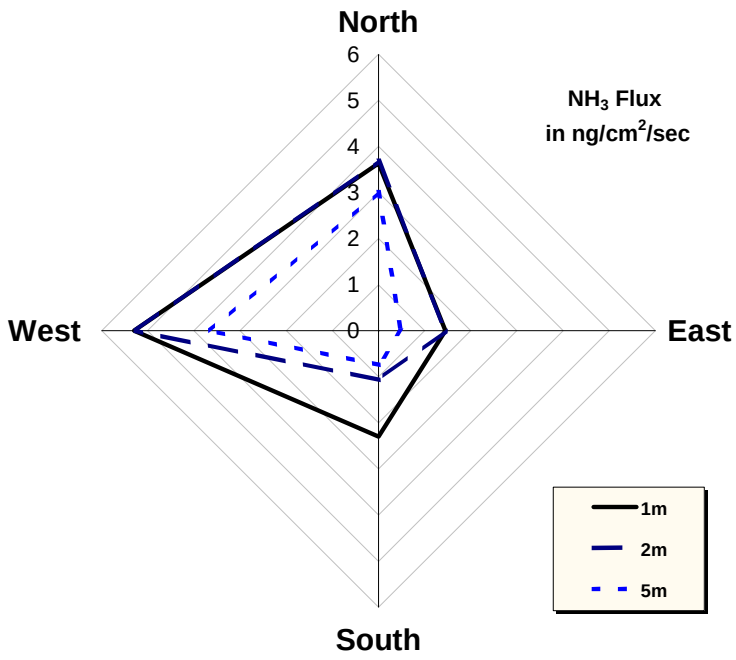

Figure 3-20. Spider plot showing the ammonia flux the day after application of fertilizer to a field at the field entrance.

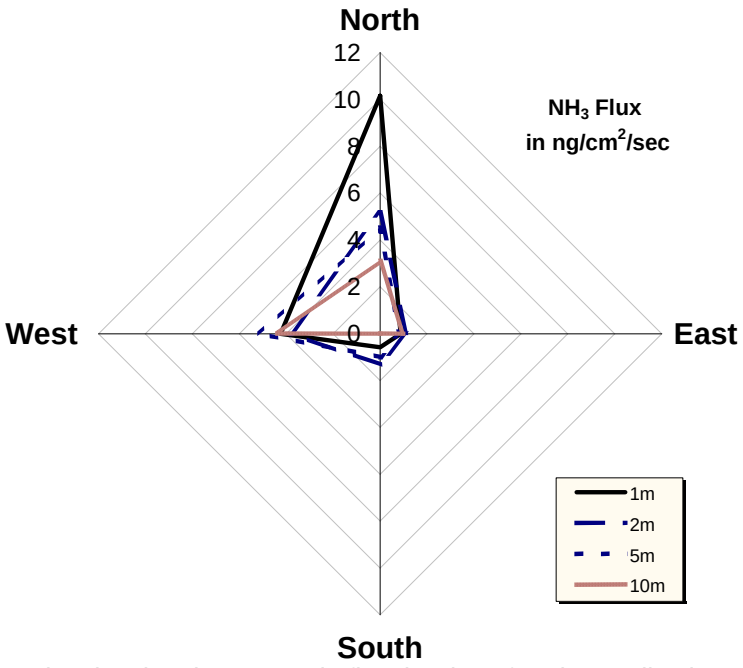

Figure 3-21. Spider plot showing the ammonia flux the day after the application of fertilizer to a field at the center of the field.

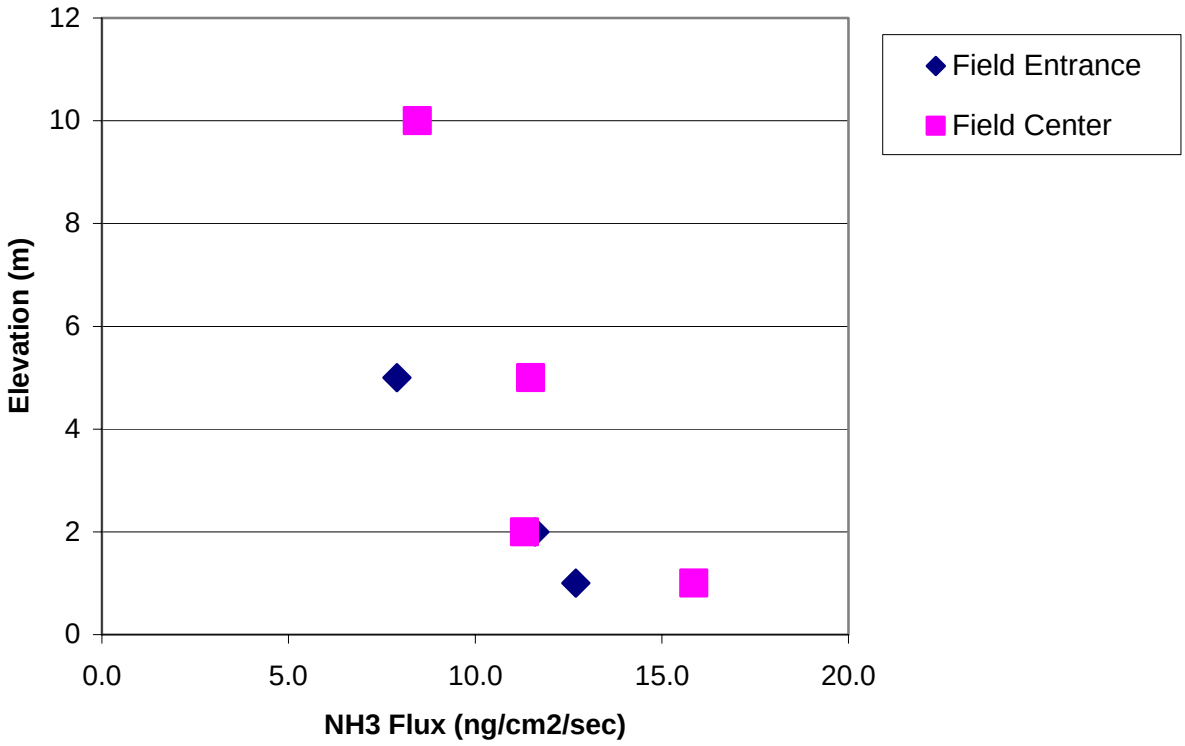

Figure 3-22. Ammonia flux profile the day after application of lagoon effluent to a field at the two measured locations.

4.0 DISCUSSION

4.1 Comparison of Collocated Passive Denuder Samples

To estimate the error for the passive samplers, two sets of passive samplers were collocated at the 2 m elevation for two of the sample measurements. The individual 16 fabric denuders from the primary denuder set used for the flux analysis were compared with the collocated set as shown in Figure 4-1. The individual denuders show a very strong correlation (r^2=0.984). The offset of approximately 13% between the two is likely from inconsistencies in the phosphoric acid coating and sample analysis. The strong correlation is especially evident in the directions where there was a stronger flux component.

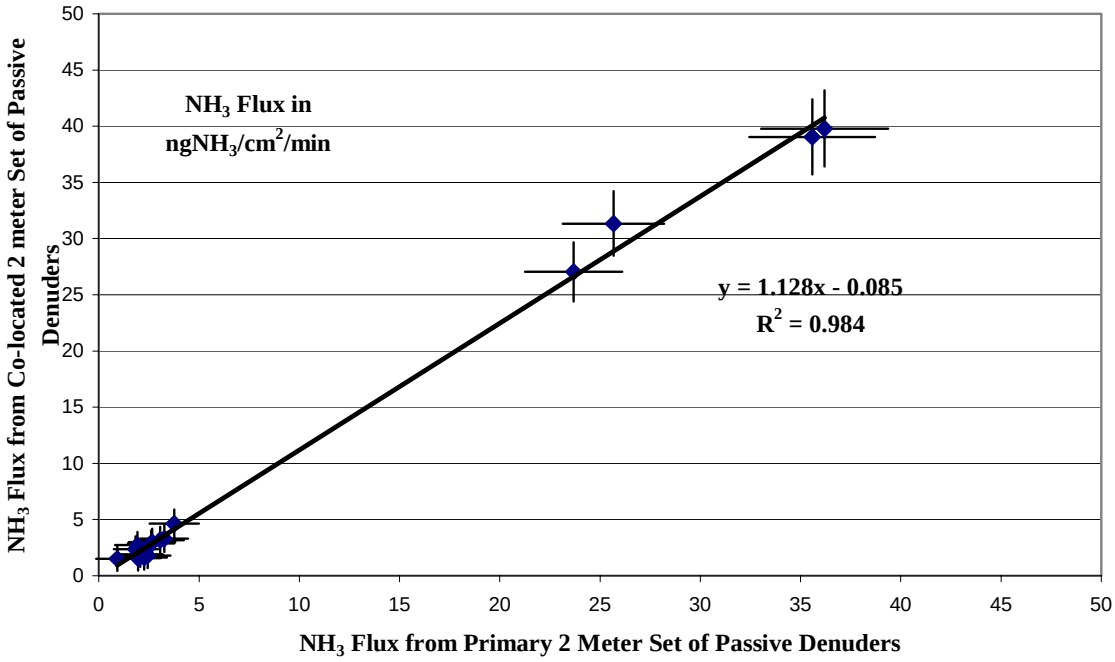

Figure 4-1. Ammonia flux from collocated passive flux denuder samples.

4.2 Denuder Efficiency

To estimate at what level diffusion predominates over the actual sample air from the source, we plotted denuder efficiency versus net flux. It is expected that net denuder efficiency becomes lower as diffusive elements affect both of the denuders for each direction. Figure 4-2 shows that when the net flux is below 2 (ng/cm^2)/min, the average denuder efficiency is less than 64%.

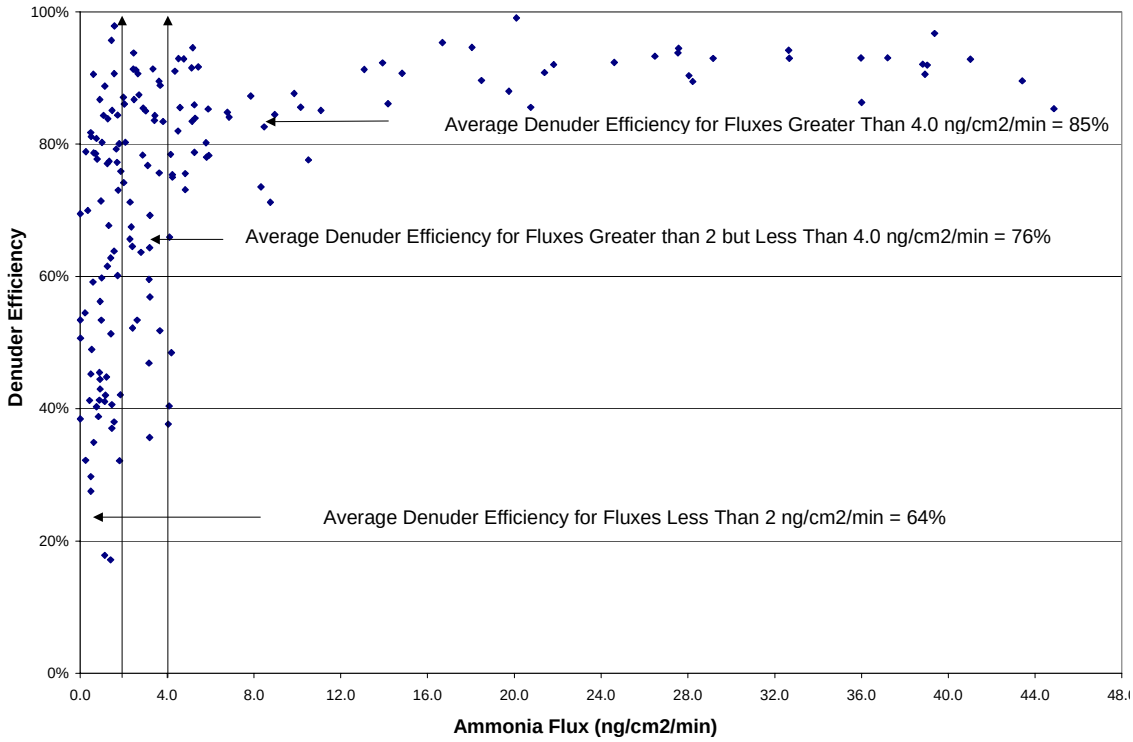

Figure 4-2. Denuder efficiency versus ammonia flux as measured using the passive flux sampler.

The average value of the flux in this range was 1.0 (ng/cm^2)/min with a standard deviation of 0.5. The average efficiency had a standard deviation of 21%. When the net flux is measured to be greater than 2 (ng/cm^2)/min but less than 4 (ng/cm^2)/min, the average denuder efficiency increases to 76% with a standard deviation of 19%. Lastly, for values of ammonia flux greater than 4 (ng/cm^2)/min, the average denuder efficiency increases to 85% with a standard deviation less than 9%. The results indicate that diffusive sources contribute anywhere from 1 to 4 (ng/cm^2)/min and are likely dependent on the background levels.

4.3 Comparison Between Active and Passive Samplers

The data from both the active and passive samplers were tabulated and are shown in Table 4-1. The active data are calculated by monitoring the cubic meters of air flow through the sample traps and multiplying the lab analysis of NH_3 on the filter by the volume of air through the filter, this results in the concentration in micrograms of NH_3 per cubic meter of sampled air. The wind speed is monitored at each elevation, and values are averaged for the sampling period. The

sample concentration of NH_3 in micrograms/cubic meter of air is multiplied by the average wind speed in meters/second to get the NH_3 flux in µg of $NH_3/m^2/s$ in the air at that elevation during that specific sampling period. These are then converted to similar units of the passive flux sampler for direct comparison.

Table 4-1. Results of passive denuder sampling compared with filter pack active sampling including pertinent meteorological parameters.

Count	Description	Height (meters)	Active (ngNH3/cm2/min)	Passive (ngNH3/cm2/min)	Ratio	Wind Speed (meters/sec)	[NH3] (micrograms/M3)	Wind Dir degrees
1	Pre-acid	1	991.7	52.5	18.9	1.12	147.9	292.9
2	Pre-acid	2	1026.4	59.1	17.4	2.01	85.0	291.6
3	Pre-acid	5	592.6	40.7	14.6	2.10	47.0	297.0
4	During acid	1	1031.2	70.2	14.7	1.83	93.8	300.7
5	During acid	2	946.9	63.2	15.0	2.91	54.3	297.1
6	During acid	5	804.1	42.3	19.0	3.08	43.4	303.2
7	Post acid	1	509.5	19.2	26.6	0.94	90.5	240.6
8	Post acid	2	391.5	15.1	25.9	1.25	52.1	237.0
9	Post acid	5	242.7	10.2	23.8	1.12	36.2	242.9
10	Dairy 1	1	1418.3	61.5	23.1	2.91	81.4	292.9
11	Dairy 1	2	1094.8	56.6	19.4	3.08	59.2	291.6
12	Dairy 1	5	839.2	38.5	21.8	1.12	125.2	297.0
13	Dairy 2	1	1798.9	82.3	21.9	2.01	149.0	300.7
14	Dairy 2	2	1282.2	85.1	15.1	2.10	101.7	297.1
15	Dairy 2	5	903.5	26.8	33.8	1.83	82.2	303.2
16	Pig 125	1	677.0	20.8	32.5	2.51	44.9	282.9
17	Pig 125	2	652.2	21.2	30.7	3.34	32.6	310.1
18	Pig 125	5	152.2	5.8	26.2	4.22	6.0	314.3
19	Pig 50	1	1015.5	41.7	24.3	2.80	60.4	305.9
20	Pig 50	2	1077.1	38.2	28.2	3.44	52.2	307.5
21	Pig 50	5	902.7	24.1	37.5	4.31	34.9	310.8
22	Pig 50	10	397.8	12.6	31.5	4.53	14.6	300.1
23	Fert 1 Ent	1	452.3	11.4	39.6	1.70	44.3	153.3
24	Fert 1 Ent	2	281.2	7.2	38.8	2.12	22.1	149.0
25	Fert 1 Ent	5	301.6	6.9	43.9	2.79	18.0	155.1
26	Fert 2 Ent	1	278.5	12.7	22.0	1.03	45.1	208.7
27	Fert 2 Ent	2	299.9	11.5	26.0	1.20	41.7	215.4
28	Fert 2 Ent	5	159.8	7.9	20.3	1.41	18.9	208.6
29	Fert 2 Cent	1	245.0	15.9	15.4	1.05	39.0	217.7
30	Fert 2 Cent	2	175.7	11.4	15.4	1.22	23.9	223.0
31	Fert 2 Cent	5	214.0	11.5	18.6	1.45	24.6	217.5
32	Fert 2 Cent	10	216.6	8.5	25.6	1.55	23.3	210.0

Figure 4-3 shows a plot of the 32 data points scaled differently by a factor of 20. The trend is quite consistent between the two. By plotting the data against each other, the plot in Figure 4-4 shows that they are significantly correlated (r^2=0.830). The average difference between the two is 24.6, with a standard deviation of 8.1. Note that the intercept on the regression line does not go through zero (3.169), and is likely not an artifact as there is no net zero, due to the effects of diffusion, taken into account for the active data.

Although this ratio exceeds the predicted laboratory results of approximately 11, many factors could bias the results of the passive sampler being low. First, at the lagoon, most of the wind came from the northwest at approximately 290 to 300 degrees, and was not directly into the face of the denuders. If we assume just a cosine function on the wind direction, this would increase the ratio from 11 to approximately 15.5. The ratio is also biased high due to the inclusion of the fertilized field data, which were clearly at such low levels that the amount of net ammonia flux was primarily less than 4.0 (ng/cm^2)/min. Also, the passive denuders and active samplers were both sampled for a period of approximately 4 hours for each of the measurements. Since the flux from the active sampler represents an average of the concentration multiplied by an average of the wind speed, discrepancies are likely. The effects of turbulence also need to be further investigated on the passive sampler. Finally, filter packs absorb particulate ammonium nitrate, and the nitrate ion then will likely partially volatilize, leaving behind ammonium ions. This is an artifact biasing filter ammonia measurements high. The variance due to diffusive effects was found to be approximately 1 ngNH_3/cm^2/min, so the uncertainty depicted in Figure 4-4 for the passive samples are Φ_{NH3} ± (.065(Φ_{NH3})+1).

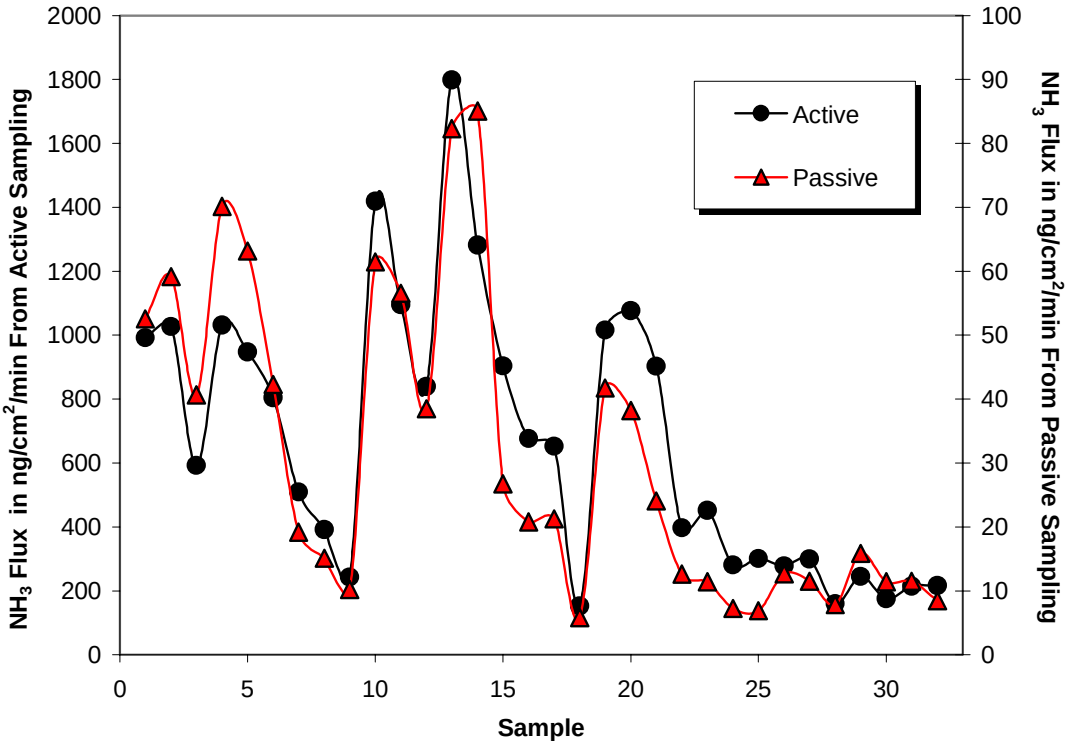

Figure 4-3. Comparison of active filter pack sampling with the passive denuder samples for the 32 different samples measured during the field program.

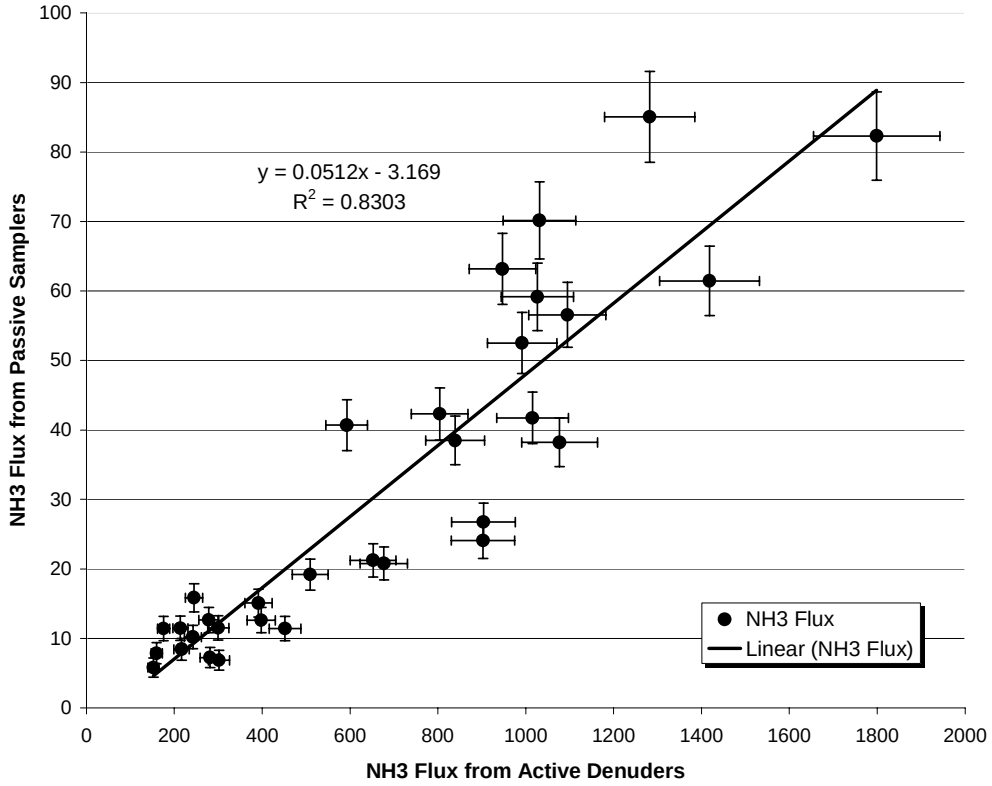

Figure 4-4. Linear regression plot showing comparison of active filter pack sampling with the passive denuder samples for the 32 different samples measured during the field program.

Active samples were tested and shown to have cumulative errors based on the flow measurement, wind speed measurement, and inconsistencies of the citric acid coating and filter analysis. Overall there is no consideration to diffusive variance, and the data on Figure 4-4 for the active samples are $\Phi_{NH3} \pm 0.08(\Phi_{NH3})$.

4.4 Emission Factors

The data from both the active and passive samplers were tabulated and are shown in Table 4-2. The available active and passive sampler data, sampled at various height intervals, was integrated vertically from the ground to the top of the plume for each of the 11 experiments. The emission flux determined for the lowest sampling height was used to represent the flux between that height and the ground. The average of the flux determined at each of two consecutive sampling heights was used to determine the flux between those two heights. The trend of the data

from the top two samples was used to determine the top of the plume. In cases where the top of the plume was determined to be greater than 25 m, the top was assumed to be at 25 m. Results are presented in terms of mass per time per unit width (crosswind dimension of source) and in terms of mass per time per unit width per unit fetch (upwind dimension of source). These results are presented for both passive and active samplers with the ratio between active and passive samplers.

Table 4-2. Results of emission factors for passive denuder sampling compared with active sampling.

Description	Passive	Passive	Active	Active	Ratio
	ng/min/cm	ng/min/cm2	ng/min/cm	ng/min/cm2	Active/Passive
Pre-acid	3.93E+04	2.78E+03	5.64E+05	3.99E+04	14
During acid	4.24E+04	3.00E+03	1.14E+06	8.09E+04	27
Post acid	1.06E+04	7.52E+02	2.51E+05	1.77E+04	24
Dairy 1	3.86E+04	1.54E+02	9.71E+05	3.88E+03	25
Dairy 2	3.52E+04	1.41E+02	9.85E+05	3.94E+03	28
Pig 125	8.57E+03	4.30E+01	2.62E+05	1.31E+03	31
Pig 50	3.02E+04	1.51E+02	9.07E+05	4.53E+03	30
Fert 1 Ent	1.54E+04	5.72E+02	9.08E+05	3.37E+04	59
Fert 2 Ent	7.94E+03	2.95E+02	1.53E+05	5.69E+03	19
Fert 2 Cent	1.73E+04	6.41E+02	5.42E+05	2.01E+04	31
Citrus Grove	1.02E+05	4.64E+02	7.51E+05	3.42E+03	7

The ratios between the emission factors determined by this approximation vary from 7 to 59. The average factor difference is 26.8 with a standard deviation of 13.1. The average factor differences for the comparison of the active and passive flux samplings were 24.6 with a standard deviation of 8.1. The increase in standard deviation is not due to discrepancies from active and passive sampling but more likely that this method is not an adequate solution for estimating the emission rate. A better method for estimating the emission rate may be to do some type of dispersion modeling of the line source.

5.0 SUMMARY AND CONCLUSIONS

A poster based on this research was presented at the International Symposium on "Passive Sampling of Gaseous Air Pollutants in Ecological Effects Research," April 9-12, 2001, in Riverside, CA, and was well received. The poster, included as Appendix D, showed preliminary data on the dairy farm and dairy lagoon measurements.

The major interest about the information presented during the poster session was that this was a direct flux measurement and in effect did not require active and meteorological sampling. The concern was that although there was strong correlation between the flux measurements from the passive flux sampler to that of the active measurements, the large multiplicative factor between the two required a more systematic approach in establishing why this was so and how this could eventually be corrected.

Many at the symposium concluded that the passive flux denuder has shown to have *the potential* to be an accurate and economical method to measure ammonia fluxes from area sources. This work was undertaken to investigate just that. A feasible first design for a passive flux sampler using fabric denuders was successfully undertaken.

During the course of this work field measurements of five independent sources of ammonia using the passive flux samplers were taken and more than 700 passive denuder samples were analyzed. With such a large number of denuders to be analyzed, procedures were written to ensure that the analysis and handling of the fabric denuders were consistent throughout the study.

Experiments were done to investigate whether collocated samples yielded similar results. From the strong correlation of these collocated samples, these results indicate the reproducibility of the results from the individual denuder samples.

The field measurements not only provided a means to estimate ammonia emissions from fugitive sources but were conducted with corresponding active samples. By comparing the active sampling concentrations with the necessary meteorological data, a comparison of NH_3 fluxes as determined by passive flux denuders with those determined by the active sampling technique was conducted. The strong correlation between the active filter pack and the passive flux

sampler, with a coefficient squared of 0.83, indicates that the passive sampling technique can provide data quality comparable to that of the active filter pack sampling.

We did not expect perfect correlation between the active filter pack sampling data and the passive flux sampler. Since the passive sampler only measures the flux and does not use a measured average wind speed multiplied by the concentration, as required in determining the flux by active sampling, we would expect to see some differences. This, however, was as significant a concern in that the slope of the regression is only 0.051, with the flux calculated by the passive denuder being much lower. This discrepancy needs to be further investigated and identified.

The large scale of the difference, on average by a factor of 20, is clearly a combination of the abatement of the flow through the present design of the flux sampler and changes in wind direction. The tested values of flow abatement, of approximately 11 over the range of wind speeds measured, is likely even higher since the tests were conducted with flow direction collinear to the direction of the flux sampler.

The data from the flux samplers were used to give an estimation of NH_3 emissions from the fugitive sources investigated. Although it is clear that at times we did not measure to the extent of the plume, analysis of the emission rates from the fugitive sources were comparable to those yielded by active sampling techniques.

The validity of the technique as a method to enhance the ammonia emission inventories requires further development of the sampler itself as well as a better understanding of the behavior of the emission from the source. For example, the localized source of the dairy lagoon clearly showed that the net flux from the lagoon was reduced by the acidification process. The estimation of the emission rate from this type of source for an inventory database would require the knowledge of the dairy practices on average that any of these types of farms undertake.

6.0 RECOMMENDATIONS

Although the passive flux denuder was shown to be an economical method of measuring NH_3 emission rates, future work should design the sampler so fewer denuder samples per sampler are required and so the sampler can be configured independently of wind direction or speed. It is likely that by redesigning the passive flux sampler to one that has the fabric denuders mounted on a wind vane type assembly, these objectives could be met.

Using the wind vane approach, the ammonium collected on the downwind side would be representative of passive sampling of concentration without wind and would be subtracted from the ammonium on the side facing the wind. This arrangement would require only four denuders rather than eight per sample. In addition, both the front and back denuders could be co-extracted and analyzed together since breakthrough does not appear to be significant. This vane approach should again be compared with flux measured using active samplers to determine if one aspect of the remaining discrepancy between the two methods can be resolved. To determine emission factors, this approach would still require samples upwind of the source, multiple sampling locations downwind of the source, and sampling at various heights up to or close to the top of the source plume.

In addition to wind vane mounting, it is likely that improving the aerodynamic design of the inlet of the passive flux sampler would allow the wind speed inside the sampler to be closer to the wind speed outside the sampler. This could be done, for example by designing the inlet with rounded edges much like jet aircraft inlet systems, or perhaps a bell-shaped inlet.

The passive flux sampler and the active filter pack sampling are different techniques. Ultimately, the goal of emission rate determination, which requires an understanding of the type of source, would better be served by comparing more sampling episodes with that of real time averaged emission rates determined by spectroscopic type methods. Both FTIR (Fourier Transform Infrared) and TDL (Tunable Diode Laser) spectroscopic techniques have the sensitivity and the response time necessary to facilitate thorough evaluation of these two types of sampling methods. The fast response of the ammonia concentrations by either of these two types of spectroscopic techniques as well as having real time meteorological data over an open path type arrangement as well as at a point source would lead to better understanding of the nature of the sources of ammonia investigated.

7.0 REFERENCES

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APPENDIX A

Procedures for Ammonia Determination

All glassware to be used for the quantitative trace ammonia analysis has to be absolutely clean. Therefore rinse all the flasks and beakers with DI or distilled water just before using them.

I. Reagents

A. Preparation of buffer solution

1) 15 g of sodium phosphate, 15 g of sodium citrate tribasic, and 1.5 g of EDTA (disodium salt) are added to a 500 ml volumetric flask.
2) The flask is filled with DI water to the line.

B. Preparation of indophenol reagent

Phenol is highly toxic and carcinogenic. All manipulations of phenol or phenol containing solutions have to be performed in a hood wearing gloves.

1) About 450 ml of the buffer solution (A) are filled into a 500 ml volumetric flask.
2) 30 g of phenol and 0.1 g of sodium nitroprusside are added to the flask and dissolved in the buffer solution.
3) The 500 ml volumetric flask is filled to the line with the remaining buffer solution.
4) The indophenol reagent is stored in a dark bottle in a refrigerator

C. Preparation of 1N sodium hydroxide solution

1) 20 g of sodium hydroxide are added to a 500 ml volumetric flask.
2) The flask is filled with DI water to the line.

D. Preparation of alkaline hypochlorite reagent

1) 400 ml of the 1N sodium hydroxide solution (C) are added to a 1000 ml volumetric flask.
2) 30 ml of commercial chlorine bleach (or sodium hypochlorite solution with 3.5% available chlorine) are added to the flask.
3) The flask is filled with DI water to the line.

II. Standards

Ammonium chloride, which is used to prepare the calibration standards, is highly hygroscopic. For an accurate calibration it has to be absolutely dry. This is accomplished by drying it for at least one hour at 100°C before weighing. Once the ammonium chloride is dry, try to keep it that way by appropriate storage, for example in an evacuated desiccator over silica gel.

E. Preparation of 1000 mgN/l ammonia nitrogen standard

1) 3.819 g of dried ammonium chloride are added to a 1000 ml volumetric flask.
2) The flask is filled with DI water to the line.

F. Preparation of 10 mgN/l ammonia nitrogen standard

1) 10 ml of the 1000 mgN/l ammonia nitrogen standard (E) are added to a 1000 ml volumetric flask.
2) The flask is filled with DI water to the line.

G. Preparation of 1 mgN/l ammonia nitrogen standard

1) 10 ml of the 10 mgN/l ammonia nitrogen standard (F) are added to a 100 ml volumetric flask.
2) The flask is filled with DI water to the line.

III. Calibration

1) 0, 2, 4, 6, 8, and 10 ml of the 1 mgN/l ammonia nitrogen standard (G), respectively, are each added to a clean 100 ml beaker.
2) 10, 8, 6, 4, 2, and 0 ml of DI water, respectively, are added to each beaker, so that the total volume of the solution in each of the six beakers is 10 ml. This results in six solutions containing 0, 0.2, 0.4, 0.6, 0.8, and 1.0 mgN/l, respectively.
3) 4.0 ml of the indophenol reagent (B) are added to each beaker.
4) 6.0 ml of the alkaline hypochlorite reagent (D) are added to each beaker.
5) The beakers are swirled and set aside for 45 min.
6) After this 45 min each solution is transferred to a 1 cm cuvette and measured three times in a VIS spectrophotometer set at a wavelength of 635 nm.
7) Prepare a calibration curve of nitrogen concentration versus absorbance including the 0 mgN/l solution.

IV. Sample analysis

1) 10 ml of DI water are added to each of the tubes with the filters.
2) The tubes are sealed.
3) The tubes are placed on a shaker table for one hour.
4) After one hour on the shaker table the solutions from each tube are poured into 100 ml beakers.
5) 4.0 ml of the indophenol reagent (B) are added to each beaker.
6) 6.0 ml of the alkaline hypochlorite reagent (D) are added to each beaker.
7) The beakers are swirled and set aside for 45 min.

8) After this 45 min each solution is transferred to a 1 cm cuvette and measured three times in a VIS spectrophotometer set at a wavelength of 635 nm

9) Any sample with an absorbance reading of greater than 1.00 is diluted and tested again.

10) Compare the measured absorbance with the calibration curve to determine the nitrogen concentration.

V. Required Chemicals

- deionized or distilled water H_2O CAS *[7732-18-5]*
- sodium phosphate $Na_3PO_3 \cdot 12\ H_2O$ CAS *[10101-89-0]*
- sodium citrate tribasic $Na_3C_6H_5O_7 \cdot 2\ H_2O$ CAS *[6132-04-3]*
- EDTA, disodium salt $Na_2C_{10}H_{14}N_2O_8 \cdot 2\ H_2O$ CAS *[6381-92-6]*
- Phenol C_6H_5OH CAS *[108-95-2]*
- sodium nitroprusside $Na_2Fe(CN)_5NO \cdot 2\ H_2O$ CAS *[13755-38-9]*
- sodium hydroxide NaOH CAS *[1310-73-2]*
- commercial chlorine bleach or sodium hypochlorite solution, 3.5% available chlorine CAS *[7681-52-9]*
- ammonium chloride NH_4Cl CAS *[12125-02-9]*

VI. Required utensils

miscellaneous spatulas
miscellaneous funnels
misc. weighing boats or dishes
pipette filler
1 cm cuvettes (lots)
VIS spectrophotometer
balance with mg precision
refrigerator
1000 ml volumetric flasks (3)
500 ml volumetric flasks (3)
100 ml volumetric flask
500 ml amber glass bottle
10 ml volumetric pipette
10 ml measuring pipette
500 ml measuring cylinder
50 ml measuring cylinder
100 ml beakers (lots)

VII. Literature

Scheiner, D.: Determination of Ammonia and Kjeldahl Nitrogen by Indophenol Method, *Water Research*, **10**(1), 31-36.

APPENDIX B

University of California, Riverside
Center for Environmental Research and Technology
Station Check

Item Checked	Reference	Range	Data
Station / General			
Date	MM/DD/YY	Equal to reference	
Time	HH:MM	Equal to reference	
Site	Name	Equal to reference	
Check By	Name	Equal to reference	
Meteorological Measurements			
Tower	intact	Yes / No	
Sensors	intact	Yes / No	
Wind direction observed (WD1)	vane direction	0 to 360 deg	
Wind direction DAS (WD2)	DAS display	0 to 360 deg	
WD1 - WD2	0 degrees	-20 to +20 degrees	
Wind speed observed (WS1)	Reference sensor	0 to 50 m/s	
Wind speed DAS (WS2)	DAS display	0 to 50 m/s	
WS1 - WS2	0 m/s	-2 to +2 m/s	
Temperature observed (T1)	Reference sensor	-10 to +50 deg C.	
Temperature DAS (T2)	DAS display	-10 to +50 deg C.	
T1 - T2	0 deg C	-2 to +2 deg C.	

Comments:

Relative Humidity Sensor

APPENDIX C

Project 18395 (CARB Ammonia) Passive Denuder Sampling Form

COLLEGE OF ENGINEERING-CENTER FOR ENVIRONMENTAL RESEARCH AND TECHNOLOGY
Atmospheric Processes Group
University of California, Riverside CA 92521-0430, 909-781-5796

Site: _____

Date _____

Field Tech: _____

Sample Elevation #1

Holder #	Front Denuder #	Back Denuder #	Start Time xxxx hours	End Time xxxx hours	Comments
N	CAP11NF	CAP11NB			
S	CAP11SF	CAP11SB			
E	CAP11EF	CAP11EB			
W	CAP11WF	CAP11WB			

Sample Elevation #2

Holder #	Front Denuder #	Back Denuder #	Start Time xxxx hours	End Time xxxx hours	Comments
N	CAP12NF	CAP12NB			
S	CAP12SF	CAP12SB			
E	CAP12EF	CAP12EB			
W	CAP12WF	CAP12WB			

Sample Elevation #3

Holder #	Front Denuder #	Back Denuder #	Start Time xxxx hours	End Time xxxx hours	Comments
N	CAP13NF	CAP13NB			
S	CAP13SF	CAP13SB			
E	CAP13EF	CAP13EB			
W	CAP13WF	CAP13WB			

Sample Elevation #4

Holder #	Front Denuder #	Back Denuder #	Start Time xxxx hours	End Time xxxx hours	Comments
N	CAP14NF	CAP14NB			
S	CAP14SF	CAP14SB			
E	CAP14EF	CAP14EB			
W	CAP14WF	CAP14WB			

Sample Elevation #5

Holder #	Front Denuder #	Back Denuder #	Start Time xxxx hours	End Time xxxx hours	Comments
N	CAP15NF	CAP15NB			
S	CAP15SF	CAP15SB			
E	CAP15EF	CAP15EB			
W	CAP15WF	CAP15WB			

Sample Elevation #6

Holder #	Front Denuder #	Back Denuder #	Start Time xxxx hours	End Time xxxx hours	Comments
N	CAP16NF	CAP16NB			
S	CAP16SF	CAP16SB			
E	CAP16EF	CAP16EB			
W	CAP16WF	CAP16WB			

Sample Collocated at Elevation:____

Holder #	Front Denuder #	Back Denuder #	Start Time xxxx hours	End Time xxxx hours	Comments
N					
S					
E					
W					